EVALUATION OF THE USE OF A GRAPHITE INTERCALATION COMPOUND FOR THE DEVELOPMENT OF A GREY WATER RECYCLING SYSTEM BY ADSORPTION AND ELECTROCHEMICAL REGENERATION

Rukayat Oki

School of Computing, Science and Engineering

College of Science and Technology

University of Salford, Salford, UK

Submitted in Partial Fulfilment of the Requirements of the Degree of Doctor of Philosophy, October 2015

Table of Contents

List of Figures

List of Tables

Acknowledgements

I would like to express my very great appreciation to my research supervisors Professor Roger Ford, Dr Nigel Brown and Dr Prasad Tumula for their valuable and constructive suggestions during the planning and implementation of this research work. Their patient guidance and useful critique has been very much appreciated.

My grateful thanks are extended to United Utilities PLC, Arvia™ Technology and the Engineering and Physical Science Research Council (EPSRC) for their contribution and financial support which made this research project possible.

Acknowledgement go to Mr Steve Whipp for his dedicated assistance and encouragement in the early stages of my PhD. Special thanks must also go to Process Engineers at United Utilities, especially Mr Alun Rees and Mr Alexander Wise for their guidance, insightful comments and commitment to this project.

My sincere gratitude go to Mrs Ruth Murphy, Mrs Rachel Aitken, Mr David Gaskell and Miss Julie Brown at United Utilities Laboratory for their valuable support with the biological analysis as well as providing me with some analytical equipment.

I express my warm thanks to staff at Arvia™ Technology Ltd and the University of Salford for providing me with the facilities and equipment required in undertaking my PhD project. I would like to thank Mr David Sanderson, Dr Andrew Campen, Dr Nuria de las Heras and Mr Donald Eaton for their patience and unconditional support.

Finally, I would like to use this opportunity to express my gratitude to my partner and best friend Andrew Okpako who has had to bear the brunt of my frustration and has helped in proof reading my work. I am thankful for his aspiring guidance, his prayers and advice during this project. Special gratefulness goes to my family for their emotional and spiritual support. I am sincerely grateful to them for sharing their truthful and illuminating views on a number of issues although not related to the project but which has helped me to keep my sanity. Most of all, thanks to God my creator who has made the impossible possible.

Declaration

This work was done wholly while in candidature for a research degree at the University of Salford. No portion of work referred to in this thesis has been submitted in support of any other application at this University or any other university or Institution.

Confidentiality

Since the results obtained in this project may be utilised for further process development, the industrial partners involved have specified the need for sensitive information such as costs and development method of novel properties are not disclosed in this thesis. The intellectual property rights and commercial confidentiality of the project also means that the information in this thesis remain confidential and is restricted to general access in the library.

List of Abbreviations

BOD	Biological Oxygen Demand
CFU	Coliform Forming Unit
COD	Chemical Oxygen Demand
DPHR	Drainage Pipe Heat Recovery
GAC	Granular Activated Carbon
GIC	Graphite intercalation compound
HSDM	Homogeneous Surface Diffusion Model
LUB	Length of Unused Bed
MBR	Membrane Bioreactor
MENA	Middle East and North Africa
MTZ	Mass Transfer Zone
NF	Nanofiltration
PDM	Pore Diffusion Model
PSDM	Pore and Surface Diffusion Model
RBC	Rotating Biological Contactor
RE	Regeneration Efficiency
RO	Reverse Osmosis
SBR	Sequencing Batch Reactor
SGW	Synthetic Grey Water
TC	Total Coliform
TOD	Total Organic Carbon

TSS	Total Suspended Solids
TDS	Total Dissolved Solids
UF	Ultrafiltration
UASB	Up-flow Anaerobic Sludge Blanket
WHO	World Health Organisation
WRVI	Water Resource Vulnerability Index
WwTP	Wastewater Treatment Plants

List of Symbols

Symbol	Description	Units
a	Volumetric surface area	m^2/m^3
a_{vr}	Adsorption area	m^2
A	Heat transfer area	m^2
A_s	Cross-sectional area of packed bed	m^2
A_T	Total surface area of tank	m^2
b	Langmuir constant	l/mg
B	Bath volume to overflow unoccupied	l
c_p	*S*pecific heat capacity of the fluid	kJ/kg °C
C_0	Initial liquid phase concentration	mg/l
C, $C(t)$, C_t	Liquid phase concentration at time (t)	mg/l
C_e	Liquid phase equilibrium concentration	mg/l
C_s	Concentration at the surface of the adsorbent	mg/l
d_o	Outer pipe diameter	m
d_p	Diameter of adsorbent particle	m
D	Inside pipe diameter	m
D_z	Axial dispersion coefficient	m^2/s
D_s	Surface diffusion coefficient	m^2/s
D_{eff}	Effective pore diffusion coefficient	m^2/s

Symbol	Description	Units
F	Faraday's constant	C/mol
F_b	Frequency of bath usage	
F_S	Breakthrough curve symmetry factor	
F_{sh}	Frequency of usage for the shower	
F_{wb}	Frequency of usage for the wash basin	
G	Mass flowrate of the fluid in heat exchanger	kg/s
Gr	Grashof number	
h	Heat transfer coefficient	W/m^2 °C
$\bar{h}$	Average heat transfer coefficient	W/m^2 °C
h_i	Heat transfer coefficient inside pipe	W/m^2 °C
h_o	Heat transfer coefficient outside pipe	W/m^2 °C
hst	Height of the stoichiometric front	m
h_w	Heat transfer coefficient inside tank	W/m^2 °C
h_z	MTZ height	m
H	Flow-rate from taps for the wash basin	l/min
I	Electric current	A
J_f	Mass transfer flux	

Symbol	Description	Units
K	Equilibrium constant	m^3/kg
K_f	Freundlich isotherm coefficient	l/mg
K_L	Langmuir constant	l/g
Ks	Intra-particle mass transfer coefficient	m/s
K_{AB}	Adams-Bohart model constant	l/min.mg
K_{Th}	Thomas model constant	l/min.mg
K_{YN}	Yoon-Nelson rate constant	1/min
k	Thermal conductivity of fluid	W/m °C
k_c	Thermal conductivity of pipe material	W/m °C
k_f	film diffusion coefficient	m/s
k_i	Thermal conductivity of insulation material	W/m °C
k_w	Thermal conductivity of tank material	W/m °C
k_1	First-order adsorption rate constant	min^{-1}
k_2	Second-order adsorption rate constant	g/mg min
L	Length of heat transfer surface	m
m	Mass of adsorbent	g
m_c	Concentration of adsorbent	g/l

Symbol	Description	Units
m_w	Mass of water in tank	kg
M_C	Mass flowrate of mains water	kg/min
M_f	Mass flowrate of adsorbent	g/min
M_H	Mass flowrate of grey water	kg/min
M_w	Molecular weight	g/mol
n	Freundlich isotherm exponent	
n_e	Number of electrons required	
Nu	Nusselt number	
P	Power	W
ΔP	Pressure drop	Pa
Pr	Pandtl number	
q_0	Initial adsorbed phase concentration	mg/g
q_{av}	Average adsorbed phase concentration	mg/g
q_e	Adsorbed phase equilibrium concentration	mg/g
q_m	Maximum monolayer adsorbed phase concentration	mg/g
q_{max}	Maximum adsorbed phase concentration	mg/g
q_r	Adsorbed phase concentration of regenerated adsorbent	mg/g

Symbol	Description	Units
$q(t)$	Adsorbed phase concentration at time (t)	mg/g
Q	Rate of heat transfer	W/m^2
Q_A	Actual charge	C
Q_f	Volumetric flowrate of fluid	l/h (l/min)
Q_{ins}	Rate of heat transfer through insulation	W/m^2
Q_T	Theoretical charge	C
Q_{Tot}	Total heat lost from tank	W/m^2
r	Radius of adsorbent particle	m
r_i	Inside radius of heat transfer surface	m
r_o	Outside radius of heat transfer surface	m
Re	Reynolds number	
R_o	Outside scale resistance of heat exchanger coil	
R_i	Inside scale resistances of heat exchanger coil	
S	Initial adsorption rate constant	mg/g min
Sh	Average flow-rate from shower	l/min
t	Time	s
t_b	Breakthrough time	s

Symbol	Description	Units
t_s	Bed saturation time	s
t_{st}	Stoichiometric time	s
t_{sh}	Average length of time in shower	min
t_{wb}	Average length of time tap is used	min
t_z	MTZ time	s
T	Temperature of fluid	°C
T_A	Atmospheric temperature	°C
T_{final}	Final temperature of fluid in tank	°C
T_i	Inlet temperature of fluid	°C
T_{iC}	Mains water inlet temperature	°C
T_{iH}	Grey water inlet temperature	°C
$T_{initial}$	Initial temperature of fluid in tank	°C
T_L	Wet wall temperature	°C
T_o	Outlet temperature of fluid	°C
T_{oC}	Mains water outlet temperature	°C
T_{oH}	Grey water outlet temperature	°C
T_s/T_{surf}	Temperature of heat transfer surface	°C

Symbol	Description	Units
T_v	Dry wall temperature	°C
ΔT_m	log mean temperature difference	
u	Superficial velocity	m/s
U	Overall heat transfer coefficient	W/m^2 °C
U_T	Total overall heat transfer coefficient	W/m^2 °C
v	Interstitial velocity	kg/m^{2}s
v_z	Traveling velocity of the MTZ	
V	Volume of solution	l
V_b	Breakthrough volume of packed bed	l
V_{sat}	Saturation volume of packed bed	l
x	Heat transfer distance	m
x_i	Thickness of insulation material	m
x_w	Thickness of tank wall	m
Y_G	Volume of water discharge	l
Z	Mass transfer distance	m
z_b	Bed height	m

Symbol	Description	Units
μ	Viscosity of fluid	mPa. s
ε	Packed bed void volume fraction/porosity	
ε_r	Emissivity of a radiating body	
ρ	Density of fluid	kg/m^3
ρ_b	Bulk density of adsorbent	kg/m^3
ρ_p	Density of adsorbent particle	kg/m^3
τ	Time required for 50% breakthrough	min
σ	Stefan-Boltzmann constant	$W/m^2\ °C^4$
δ	Number of individuals/users	

Abstract

Grey water recycling has become of increasing interest as a water conservation method to help reduce the stress on water resources. This thesis evaluates the effectiveness of an innovative process in treating grey water for reuse for commercial and residential purposes as well as the possibility of heat recovery from the grey water. The process investigated is based on two fundamental elements; adsorption of contaminants onto a patented graphite intercalation compound (GIC) supplied under the trade name of Nyex™, and electrochemical regeneration of Nyex™ both taking place within a single unit.

The adsorption characteristics of Nyex™ was initially evaluated by conducting an adsorption isotherm and adsorption kinetics experimental study. Electrochemical regeneration of Nyex™ saturated with contaminants from grey water was also studied using an electrochemical cell. Results from this work has for the first time demonstrated that Nyex™ is only able to adsorb organic contaminants from grey water. The uptake of organic contaminants onto Nyex™ took place within a minute and the rate of adsorption was best described by the pseudo-second order adsorption kinetics. Adsorption isotherm curves illustrated multi-layer adsorption of organic contaminants onto Nyex™ with a monolayer adsorption capacity of 15 mg/g COD. An adsorption isotherm study conducted for anionic surfactant showed only monolayer arrangement of anionic surfactant molecules with a monolayer adsorption capacity of 0.3 mg/g.

Regeneration of the adsorbent is achieved by electrochemical oxidation in the anode compartment of an electrochemical cell. Complete regeneration of the adsorbent to its full adsorption capacity was achieved with a minimum charge of 22 C/g, and this capability was maintained over repeated regeneration cycles. A 4-log reduction in coliform through disinfection by free chlorine generated from the electro-chlorination process was observed, thus indicating that the system is highly effective at disinfection. A theoretical design of a drainage pipe heat recovery unit showed that it is possible to preheat mains water from 8°C to 25°C, using a heat exchanger coil of around 1 metre long. Evaluation of the operating cost as well as the cost savings from water and heat recovery suggests that this technology is economically viable and thus could be a major player in the grey water recycling market.

Description of Thesis Structure

In order to coherently present the information gathered and generated throughout the duration of this research project, the thesis has been structured into five parts and each part is further divided into chapters.

Part 1 – Introduction

The first part of the thesis introduces the project and the Arvia™ technology, it also puts the project in context introducing the problem and the project objectives as well as defining the scope of the project. Specific topics covered within chapters in the introduction includes project motivation, rational and project scope.

Part 2 – Literature Review

This section focuses on the key areas of understanding pertinent to the development of the technology. It includes an introduction to grey water recycling as well as legislative requirements for such use. An in depth study of the adsorption and electrochemical regeneration process is also covered in this section, along with a review of the characteristics of Nyex™ and heat recovery process.

Part 3 – Material and Methodology

The materials (adsorbent and adsorbate) used for the experimental work are discussed in this section. The experimental and analytical methods used to investigate the adsorption and regeneration properties of the process are also discussed.

Part 4 – Results and Discussion

This section covers the technical content of this work, presenting data obtained from the treatment of synthetic grey water using the Arvia™ process. The first chapter investigates the adsorption capabilities and characteristics of the Nyex™ adsorbent in a batch mode process. This is followed by a review of the capability of the regeneration of Nyex™ saturated with contaminants from grey water by electrochemical regeneration. The next chapter investigates the effectiveness of treatment by continuous adsorption and electrochemical regeneration and then a discussion on the disinfection of grey water focusing on the mechanism of disinfection.

The design of a heat recovery unit is proposed in the final section as well as a review of the economic benefits of the system.

Part 5 – Conclusions and Future Work

Conclusions of the work undertaken in this project along with recommendations for future work are presented in this section.

CHAPTER 1: INTRODUCTION

Overview

Part 1 of this thesis aims to provide a brief introduction to the project, outlining the purpose and nature of the present research. The first section (Chapter 1.1) reviews the project background in order to highlight the importance of this project and its impact to the wider community. The intention of the first section is also to put the project into context focusing on how the issues tackled in this project have come about. The chapter then goes on to highlight current methods which have proved useful in tackling these issues and then very briefly drawing attention to the gaps in the published literature. The aims and objectives of the project is discussed in chapter 1.2 together with the expected outcome of the project. Chapter 1.3 outlines the scope of the project drawing particular attention to the limitations of this research work. Chapter 1.4 is a brief description of the Arvia™ process, the technology used in this research. The research methodology is outline in the last section of this chapter, this includes an overview of the experimental rationale and literature review.

1 INTRODUCTION

1.1 Project Background and Motivation

Climate change is altering weather and water patterns around the world, causing water shortage and drought in some areas and flooding in others (WWF 2014). In addition to this, population growth and lifestyle changes have led to an increased demand for water. At the current consumption rate, water shortage is only likely to get worse (Bogardi et al. 2012).

As water scarcity becomes a more pressing concern, water conservation is becoming more important as a partial remedy in tackling this issue. Many countries in water stressed areas trying to bridge the gap between reduced water supply and increasing demand have come to accept the importance of water reuse as a valuable step in water conservation (Whitehead and Patterson 2007). This has led to the introduction of water reuse schemes around the world (Jimenez and Asano 2008). For instance, Australia has reformed its governance system in order to adopt the use of recycled water for residential buildings (section 2.2.2.1). It plans to increase its national water reuse to 30% by 2015 (Geary et al. 2005). In the Middle East and North Africa (MENA) region, the reuse of treated wastewater for agriculture and irrigation has accelerated and is becoming increasingly important in water resource management (Qadir et al. 2010). Water reuse policy has been included in the national water portfolio within the MENA region. As an example, Egypt has reformed its policy to include guidelines for mixing drainage water with fresh water as per the regulations for water reuse and health protection measure and standards specifications (The World Bank 2011). Water reuse via rivers is well established in Europe and is used increasingly in the United State. It has led to the development of reuse guidelines in many states, designed to protect public health and the environment (Crook and Surampalli 2005). Of all the many states benefiting from water reuse, California, Texas, Florida and Arizona accounts for 90% (Water Reuse Association 2008). In Redwood California, the Recycle Water Project aims to use recycled water for landscape irrigation and currently saves around 50 million gallons of potable water each year (Redwood City 2012). Within the city of Olympia Washington, treated wastewater is reused by agencies and businesses for various non-potable use such as toilet flushing, decorative fountains and ponds, pressure washing and irrigation (City of Olympia 2014). In Japan, anti-drought legislation which makes recycling compulsory for buildings over a certain size have been put in place (Eriksson et al. 2008).

The UK also supports water reuse and the British standards Institution have recently published standards for both rainwater harvesting (British Standards Institution 2009) and grey water recycling (British Standards Institution 2010). These standards provide guidance for design, installation, and maintenance as well as treated water quality requirements.

Current water distribution systems are centralised and follows a continuous water cycle, in that, water withdrawn from aquifers or surface water body are treated and then distributed to homes and businesses. The treated water is used for various domestic and industrial purposes and is then sent to wastewater treatment works, the treated water is subsequently sent back to the environment. Including water recycling into the water cycle means that treated water initially distributed to homes and businesses can be reused with little or no treatment before sending back to wastewater treatment works. This therefore reduces the amount of water taken from the environment, thus reducing pressure on water resources which is especially beneficial for regions with very little rainfall. Water recycling also reduces pressure on water and wastewater treatment plants as less water is treated which results in reduced energy requirement.

The methods by which water can be reused are through rainwater recycling, grey water recycling and reuse of effluent from wastewater treatment plants. Rainwater recycling is the collection and recycling of rainwater for non-potable use. Rainwater recycling is the simplest method requiring no initial treatment for non-potable use, however, rainwater source is unreliable and its applicability is limited in regions affected with drought (due to low rainfall). Reusing effluents from wastewater treatment plants is not always feasible due to risk of ground water contamination (in case of pipe fracture leading to cross contamination) and the need for a separate water distribution channel which can be very costly. Grey water recycling is the reuse of water from showers/baths, sinks, washing machines and dish washers in residential or commercial buildings. Grey water represents a large wastewater source of around 70% of total wastewater generated in an occupied building, but contains only 30% and less than 20% of organics and nutrients respectively in wastewater (Pidous et al. 2007). The low contaminant level of grey water compared to wastewater means that treatment is more economical.

Recycled grey water can be used either without treatment or after disinfection for restricted re-use such subsurface irrigation and toilet flushing. Alternatively, grey water can be processed through a number of filtration, chemical, biological and disinfection treatment stages to allow for unrestricted reuse such as household cleaning and laundry. Although a more intensive treatment process allows for unrestricted reuse and poses less risk to the public, this option can

be expensive. Designing a grey water recycling technology that is cost and energy efficient, and can produce grey water for a large range of non-potable use remains a challenge. Large scale water treatment plants are not usually appropriate for treating grey water for residential or commercial use due to high distribution/pumping cost (Angelakis and Durham 2008).

Consumers are only likely to purchase a device where they could see financial return, hence, in order to attract potential buyers, it is paramount that the system is designed to suit the needs of the property and its owners. The capital cost of a grey water recycling system must be equivalent to the price of the mains water it replaces and the savings it provides for the user, as this would enable a shorter payback period. Hence, another way grey water recycling systems can be more attractive is if they satisfy other essential needs other than reduction in mains water usage. Water heating is a major part of household energy use, 24% of energy consumed within households in the UK is used for heating water (The Greenhouse Trust, 2011). Thus, if this energy can be recovered within the grey water recycling process this could produce an economic driver for the installation of such device.

There are currently several manufactures of grey water recycling systems for domestic and commercial use, all of which are trying to achieve the same goal of reducing the amount of mains potable water usage (APPENDIX F). The treatment methods for these systems comes in different levels of complexity and price ranges from a few hundred pounds for a small, simple system, to thousands of pounds for a more complex, multi-stage systems.

The simpler grey water recycling technologies often diverts the grey water with or without disinfection. However, use of grey water produced using simple treatment methods needs to be used without storage and is limited to toilet flushing and sub-surface irrigation to avoid human contact. These limitations reduce the economic benefits of the technology as a lower volume of grey water recycled means more mains water is consumed thus decreasing cost savings for consumers (Mourad et al. 2011).

The more advanced treatment systems which produce higher quality grey water fit for a wider range of uses incorporate a combination of filtration, coagulation and biological treatment processes (Antonopoulou et al. 2013, Jabornig and Favero 2013, Pidou et al. 2008, Gross et al. 2007, Parsons et al. 2000). The majority of the advanced grey water recycling technologies currently available uses a combination of membrane filtration and biological treatment methods, followed by either chlorine or UV disinfection (Pidou et al 2007, Friedler and Hadari

2006). Biological treatment processes are only able to remove organic contaminants capable of undergoing biological decomposition, and are not able to remove suspended solids which is why membrane filtration and disinfection stages are required (Friedler 2005, Nolde 2005, Al-Jayyousi 2003). Deposition of contaminants on the membrane can result in fouling of the membrane. This can have a substantial effect on the membrane performance, and frequent cleaning of the membrane will increase the operational cost of the system (Pidou 2007, Owen et al. 1995). Coagulation methods on their own are not completely successful in treating grey water. Filtration, coagulation and biological methods usually generate sludge which requires further treatment and disposal (Semerjian and Ayoub 2003). In general, none of the technologies discussed above can be operated without manual intervention or highly advanced control and automation making their cost uneconomical. The various grey water treatment methods which have so far gained research attention are discussed in more detail in APPENDIX F.

Adsorption using granular activated carbon (GAC) is a technique widely used in municipal potable water purification as well as wastewater treatment, but is a treatment method which has scarcely been applied for grey water recycling. Adsorption is the process through which soluble or partially soluble compounds accumulate on a suitable interface or surface until the amount of substance remaining in solution is in equilibrium with the amount on the surface (Faust and Aly 1987). The substance that is being adsorbed (or removed) from the liquid phase is called the *adsorbate*. The *adsorbent* is the solid material which provides the surface for the *adsorbate* (Figure 1.1). The adsorption process used in wastewater/water treatment is a mass transfer operation in that substance(s) in the liquid phase adsorbs onto the solid phase (or adsorbed phase). The driving force for this process is the reduction in the surface/interfacial tension between the liquid and adsorbed phase as well as an increase in concentration or mass gradient (Tchobanoglous et al., 2003; Faust and Aly 1987).

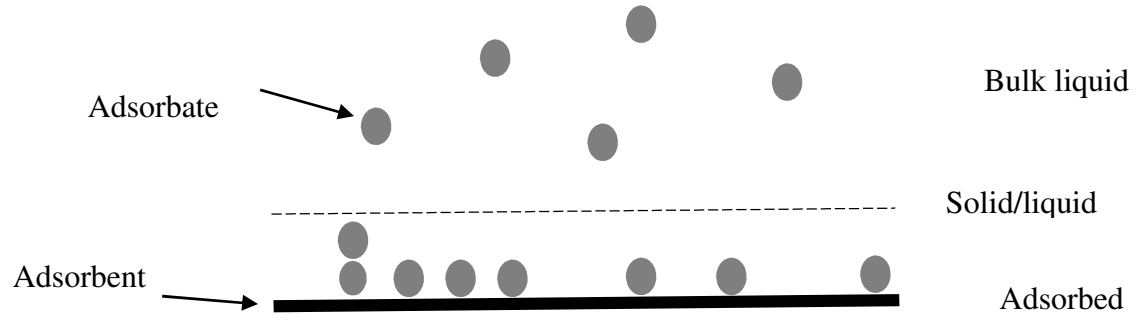


Figure 1.1 - Schematic of an adsorbent surface depicting monolayer and multilayer adsorption and the surrounding stagnant fluid film

A column (typically a tube or rectangular chamber), known as an adsorption column is used in an adsorption process to hold the adsorbent material. The adsorption column, referred to in this thesis as a packed bed column can either be fixed meaning the adsorbents are held in place and do not move, or fluidised in which the adsorbents move freely within the column). Design method for a packed bed column is discussed is section 2.4.3 of this thesis.

The feasibility and economic viability of the adsorption process depends on whether the adsorbent is disposed of or recovered (regenerated) for further use. Recovering the adsorbent for further use is much more economical and environmentally friendly. This is due to reduced material and disposal costs as well as eliminating the need to dispose of used adsorbent to landfill sites.

Thermal techniques are widely used to regenerate contaminated GAC, however, this process requires a temperature of up to 800 ºC and thus is not economically viable for smaller scale systems such as grey water recycling (Berenguer et al. 2010). Wet air oxidation is also used to regenerate contaminated activated carbon slurry through oxidation of the adsorbed contaminants. In comparison to thermal regeneration, wet air oxidation occurs at a lower temperature of 150 ºC to 320 ° C, but requires an operating pressure between 0.5 to 20 MPa which again limits its applicability for grey water recycling (Kolaczkowski et al. 1999). Chemical regeneration involves desorption of adsorbed contaminants by means of an organic or inorganic solvent. Although the process is simple and can be operated at room temperature and pressure, it is only able to achieve regeneration efficiency of below 70% and requires use of hazardous chemicals (Berenguer et al. 2010). Electrochemical regeneration technique has been found to be a feasible alternative achieving fairly high regeneration efficiency and is suitable for small and medium scale processes (Zhang 2002; Narbaitz and Cen 1994).

Electrochemical regeneration is the process by which adsorbed molecules are removed from the surface of the adsorbent with the use of electrical current within an electrochemical cell, thus restoring the adsorptive capacity of the adsorbent. The three main mechanisms by which the electrochemical regeneration process can encourage desorption of contaminants from the surface of the adsorbent are: (1) formation of ions through electrolytic dissociation, which can change the pH conditions in the cell thus affects the adsorption equilibrium, which have been shown to promote removal of contaminants; (2) reaction between ions formed on the surface of the adsorbent and adsorbed contaminants thus resulting in the formation of species with less

affinity to the adsorbent; (3) destruction of adsorbed contaminants by electric current (Das et al. 2004; Mehta and Flora 1997). These mechanisms are discussed further in section 2.6.

The low electrical conductivity and high porosity of activated carbon makes electrochemical regeneration process energy intensive and requiring high retention times (Narbaitz and Karimi-Jashni 2009; Weng and Hsu 2008; Narbaitz and Cen 1994). In order to address these issues, a patented novel non-porous, highly conductive carbon adsorbent with the trade name Nyex™, has been developed. Nyex™ is a modified graphite material known as graphite intercalation compound (GIC). GICs are complex graphite material in which guest species (intercalants) are inserted between the graphene layers. This reaction enables delocalised electrons to move more freely thus resulting in the high electrical conductivity of GICs (section 2.3). The highly conductive nature of Nyex™ adsorbent, reduces the energy required for regeneration. In addition, the non-porous nature of Nyex™ enables rapid adsorption and regeneration (Brown et al. 2004a; Brown et al 2004b).

The system tested in this research project uses continuous adsorption onto Nyex™ adsorbent and electrochemical regeneration taking place in a single cell unit. This is known as the Arvia™ process (section 1.4) and has so far not been utilised or tested for the purpose of grey water treatment. This thesis evaluates the possibility of integrating the Arvia™ process into a grey water recycling technology for residential use in the UK that is both economical and environmentally friendly. The main research questions addressed in this thesis are therefore;

1. Can Nyex™ adsorb contaminants in grey water and can Nyex™ saturated with contaminants from grey water be electrochemically regenerated?"
2. Can the Arvia™ process be integrated into the design of a grey water and energy recycling system which can be economically utilised in a typical residential home in the UK?

1.2 Project Aims and Objectives

The main aim of this research work is to design a grey water and energy recycling device that is both economical and low maintenance. As well as ensuring economical design of the grey water recycling system, another way of increasing the economic viability of the process is by recycling the heat energy in the grey water. Hence, the incorporation of heat recovery was also evaluated in the design of the grey water recycling system.

Previous research have shown Nyex™ to be an effective adsorbent which can be rapidly and economically regenerated through electrochemical regeneration (Brown et al. 2004a; Brown et al 2004b). In this research work Nyex™ has been studied for the removal of contaminants from grey water by adsorption and electrochemical regeneration technique, known as external isothermally controlled Energy House situated within a laboratory at the University of Salford. This facility was used for quantitative investigation of energy conservation and loss for a series of different configurations. A prototype of the Arvia™ process was installed in the UK's only

In order to achieve the aims of this project, the following objectives was undertaken:

- Evaluation of the adsorption kinetics and adsorption equilibrium characteristics of Nyex™ by plotting adsorption kinetics and adsorption isotherm data.
- Investigation of electrochemical regeneration of Nyex™ loaded with contaminants from grey water.
- Development of chemical engineering design model of grey water treatment by adsorption and electrochemical regeneration.
- Investigation of the possibility of heat recovery by the evaluation of possible heat recovery methods.
- Cost evaluation to determine economic viability of the proposed design
- Review of relevant regulations to ensure design is in compliance with water regulation requirements and 'by laws' governing the management of water within the home.

The objectives outlined above was aimed at the following outcomes:

- Design of a grey water and energy recycling system that can recover water and heat energy for a wide variety of reuse purposes.
- Analysis of the performance of the system to set out its potential and identify any constraints for its use.
- Provide recommendations for future work requirements based on technical assessments.

1.3 Project Scope

The research work described in this thesis focused mainly on investigating the possibility of incorporating the Arvia™ process into the design of a grey water and energy recycling system.

This involved experimental design which would enable evaluation of operating parameter such as organic and hydraulic loading. The experimental data were then analysed using appropriate models describing the adsorption and process.

Although this research work was aimed at the optimisation of the Arvia™ process in order to suit the needs of the grey water recycling system, it would not involve making changes to the patented Nyex™ adsorbent. Any suggestions for a new adsorbate would be undertaken by Arvia™ Technology Ltd.

1.4 The Arvia™ Process

Since its invention in 2001, the Arvia™ process has been well researched and has proven to be commercially attractive for removing dissolved organic contaminants. Arvia™ Technology Ltd was subsequently formed in 2007 as a spin out from the University of Manchester. The company is gradually transitioning from a purely research and development organisation to a manufacturing and services organisation with the aim of applying the Arvia™ process in both the nuclear and water sector. This research project fits in with its continuous development goal by evaluating new and innovative methods in which the Arvia™ process can be applied in the water sector.

The Arvia™ process offers several advantages including ease of operation, high removal efficiency of organic contaminants, low cost (particularly at low organics concentration) and no waste product is generated during operation. The Arvia™ process is based on a combination of two important elements: adsorption onto a patented carbon based adsorbent material (Nyex™), and an electrochemical regeneration process.

Nyex™ is a non-porous material, with high electric conductivity which means it can efficiently be electrochemically regenerated (properties of Nyex™ discussed further in section 2.3.6). The fundamental principal of the Arvia™ process is that adsorption onto Nyex™ and electrochemical regeneration of the Nyex™ material occurs simultaneously. This is achieved by passing the effluent solution through a packed bed of Nyex™ adsorbent enclosed within an electrochemical cell.

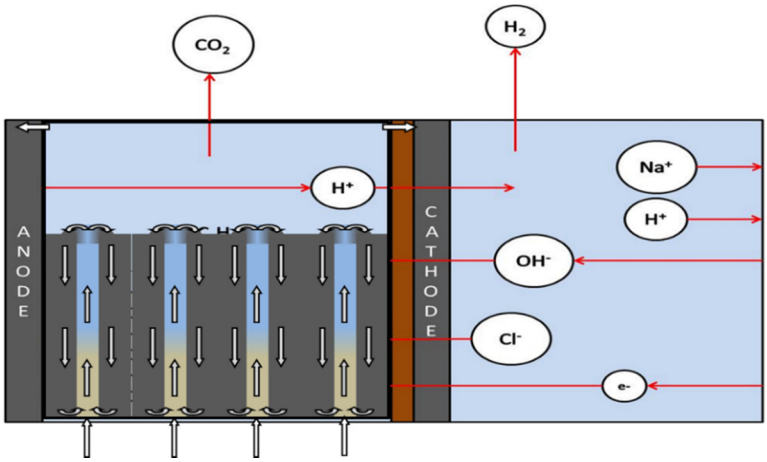


Figure 1.2 - Schematic of the electrochemical cell used for the catholyte system and an illustration of ions and gasses generated during electrochemical regeneration

The electrochemical cell is separated into anodic and cathodic compartments by a micro-porous Deramic 350 membrane. The membrane is fabricated from high molecular weight polyethylene ribbed sheet containing amorphous silica with an average electrical resistance of 0.12 Ω cm^{-2}, whilst the cathode and anode electrodes are both carbon based.

Two variation of the electrochemical cell referred to as the catholyte and non-catholyte system were used for this project. The non-catholyte system consists of a packed bed of Nyex™ on both the anode and cathode compartment; whereas for the catholyte system, the cathode compartment holds a catholyte/electrolyte solution made up of sodium chloride (Figure 1.2).

Reaction at the Cathode compartment

Reduction occurs at the cathode, hydrogen ions (H^+) flow from the anode to the cathode compartment and are reduced to hydrogen gas while water is reduced to form hydroxide ions (OH^-).

$$2H^+ + 2e^- \rightarrow H_2(g)$$
$$H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$$

Reaction at the Anode compartment

Electrochemical oxidation takes place at the anode where chloride ions transferred from the cathode compartment, are oxidised to chlorine gas. Oxidation of water and organics also occurs, generating hydrogen ions and carbon dioxide respectively.

$$2H_2O(l) \rightarrow O_2 + 4H^+ + 4e^-$$
$$4OH^- \rightarrow O_2 + 2H_2O(l) + 4e^-$$

Oxidation of Organics

$$C_X H_Y + O_2 \rightarrow CO_2(g) + H_2O(l)$$

Side Reaction

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

The Arvia™ process is potentially an effective method for the treatment of grey water because it adsorbs and regenerates rapidly, requires minimal use of chemicals, has a very simple design, can be operated at room temperature and generates no sludge hence no extra treatment is required.

1.5 Research Methodology

1.5.1 Literature Review

As highlighted in the previous section, the main processes occurring in this research work which are evaluated in the literature review includes:

- *Grey water recycling process*; defining the quality (parameters), quantity (discharge rate) and regulatory requirements is necessary in the treatment and reuse of grey water.
- *Graphite Intercalation Compound (GIC) and Adsorption process*; adsorption is a fundamental part of the removal of contaminants from grey water in this research work. Hence, a sound understanding of the phenomena is necessary in order to rationalise experimental results obtained from this work. A general understanding of GIC is also important to better appreciate the reasoning of the experimental results from the adsorption process.
- *Electrochemical regeneration process*; electrochemical regeneration was selected as the recovery method for the Nyex™ adsorbent as it has been shown to be fast, effective and economical. An understanding of the methodology is key and would enable rational for anomalous trends in the electrochemical results.

- *Heat recovery*; heat recovery is fundamental in the economic viability of a grey water recycling system. It is important therefore to understand how this can be incorporated into a residential grey water recycling system and what factors need to be considered for design.

1.5.2 Experimental Rational

The first step in designing an adsorption column using a novel adsorbent is to obtain a good understanding of the adsorption characteristics of the adsorbent, as well as evaluating the regeneration efficiency of the electrochemical regeneration process. Once this has been determined the next very important stage of the design process is an experimental study using a packed bed column to establish a breakthrough curve. The experimental method used in obtaining design data overlap with that used by other researchers focusing on adsorption and electrochemical regeneration. The following points were addressed in this research work (a more detailed description of the experimental work can be found in chapter 3).

Stage 1 – Understanding adsorption characteristics of the adsorbent

- Batch adsorption of contaminants from grey water
- Batch adsorption kinetics study
- Batch adsorption equilibrium/isotherm study
- Batch electrochemical regeneration of Nyex™ saturated with grey water contaminants

Stage 2 – Packed bed study

- Packed bed study with and without electrochemical regeneration (Combined adsorption and electrochemical regeneration in a single unit)
- Mechanism of grey water disinfection

Stage 3 – Evaluation of heat lost through the system.

Synthetic grey water was used in carrying out all experimental work in this project in order to enable reproducibility of experimental results.

1.6 Summary

Water recycling is a very important method in combating water shortage which has affected many regions around the world. Subsequently, water reuse schemes have been introduced in

many regions worldwide in order to maintain current/available water resources. Out of all available water recycling methods, grey water recycling is the most effective due to its low contaminant load and ability to meet water reuse demand. There are several processes which have been tested for treating grey water. These treatment methods are often fairly unreliable on its own, for instance chemical and biological methods typically requires a filtration and disinfection stage, and the physical/filtration treatment methods usually require a disinfection stage. Biological treatment incorporated with filtration have proven to be the most effective method. However, this method can be costly and produces sludge which has to be disposed of via sewerage, thus adding to the sewerage cost.

Adsorption process is a physical treatment method which has not been very well explored for the purpose of grey water recycling. This is likely due to the fact that the adsorbent material once used in the process need to be disposed of which makes it less effective for residential use. Regeneration of used adsorbent would be more effective but current regeneration techniques are only appropriate for industrial purpose, rather than residential use. Electrochemical regeneration is a fairly new regeneration technique which may be appropriate but requires a highly conducting environment in order for it to be economical. Nyex™ is a novel adsorbent, developed by Avia™ Technology. It is a graphite interaction compound which means it has a high electrical conductivity. Using Nyex™ in place of the often used activated carbon means that the electrochemical regeneration process can be more economical. Using Nyex™ makes it possible for adsorption and electrochemical regeneration to occur in a single unit. This process is known as the Arvia™ process. One of the aims of this research work is to investigate incorporation of the Arvia™ process into the design of a grey water recycling system. Including heat recovery into the system means that the system is more attractive to a wider range of consumers as the cost savings increases. Hence, the second part of this research work is to evaluate possible heat recovery method that is effective and economical for the system.

The scope of this project is limited to evaluating the effectiveness of the Arvia™ process in removing contaminants from grey water over an extended period of time. This includes conducting experimental studies using the Arvia™ process and making recommendations for future design. Any modifications to current work or fabrication of new design would be conducted by Arvia™ Technology.

The fundamental elements of this research work which would be evaluated in the literature review are; fundamentals of grey water recycling, adsorption processes and electrochemical regeneration process. Experimental study carried out would allow understanding of the adsorption characteristics of Nyex™ and obtaining an adsorption profile of the packed bed column for various flows, initial concentrations and electric current (during electrochemical regeneration).

CHAPTER 2:
LITERATURE REVIEW

Overview

Chapter 2 of this thesis is a review of published work concerning the subject matter in this research. Section 2.1 focuses on defining grey water as well as pinpointing its various sources. The quality and quantity of grey water is examined in section 2.1.2 and 2.1.3 respectively. Section 2.2 is a review of the process of grey water recycling. The first section emphasises the importance and impact of grey water recycling (section 2.2.1). Section 2.2.2 discusses grey water legislation in selected regions around the world, highlighting the treatment requirements which have been set out by different regulators.

Section 2.3 presents a brief introduction to graphite intercalation compounds (GICs). This is followed by a description of the intercalation method used to synthesise Nyex™ adsorbent (section 2.3.2) as well as a review of the potential use for GICs as an adsorbent (2.3.4). Section 2.4 provides a description of the fundamentals and theories of adsorption highlighting the various models used for an adsorber/packed bed design. Section 2.5 introduce the electrochemical regeneration process, focusing mainly on the electrochemical oxidation reaction which is the process used in this research. The mechanism of electrochemical oxidation is also reviewed in section 2.5.3. The final section is a review of the heat recovery process, discussing the theories and methods used for domestic heat recovery.

2 LITERATURE REVIEW

2.1 Grey Water Overview

2.1.1 Definition and Sources

Greywater generated from domestic activities can often be divided into categories depending on the level of contaminants contained in the water:

- *Light grey water* is domestic wastewater that is highly diluted thus resulting in very low contaminant levels.
- *Dark grey water* (also known as mixed grey water) consists of both light grey water plus wastewater from sinks involving food preparation.

With the appropriate treatment and disinfection, domestic wastewater can be reused for a variety of non-potable applications. Light grey water often has a low enough contaminant concentration that reuse application can be considered without the need for intensive treatment, providing the application has a low risk of direct human contact (such as subsurface irrigation), and when storage is not required. In some cases, light grey water is used for subsurface irrigation as well as for toilet flushing after only being disinfected.

Grey water is generated in every occupied residential, commercial and industrial building with a potable water supply. It contains varying levels of organic and biological contaminants, as well as grease, oils, fats, soaps, hair, lint, household cleaning products and various other chemicals. The main sources of grey water production are:

- Bathroom grey water is wastewater from baths, hand basins and showers; on average, bathroom grey water contributes to around 35-60% of domestic wastewater used in a typical household (Friedler 2004). Bathroom grey water can be contaminated with body fats, urea, faeces, hair, cleaning and personal care products such as; shampoos, conditioners, hair dyes, toothpaste, etc. as well as varying level of microorganisms through body washing. This means bathroom grey water is most likely to contain high level of surfactant with some levels of faecal coliforms. The quality of bathroom wastewater (particularly from showers) varies from a more contaminated water produced from washing off products such as soaps and shampoos to a less contaminated

water produced just from clean rinsing. Water from this source is often less contaminated and can be categorised as light grey water (Birks and Hills 2007).

- Laundry grey water contributes around 13% of household water usage (Friedler 2004). Laundry grey water is often contaminated with lint, grease, laundry detergents as well as faecal contaminants through washing soiled clothes. As with bathroom wastewater, the quality of laundry wastewater also varies in quality from wastewater produced from the wash cycle to that generated during the rinse cycle (Kaur 2010). Laundry grey water is likely to consist of high level of organic contaminants with moderate levels of anionic surfactant and faecal coliforms. Laundry grey water often falls under the light grey water category, and at times categorised as dark/mixed grey water when clothes are soiled with faeces or food waste.
- Kitchen grey water sourced mainly from dishwashers and kitchen sinks accounts for around 9% of domestic wastewater (Environmental Agency 2011). Grey water from kitchen sinks contains oil, grease, food particles and cleaning products. It contributes to the majority of biological contaminants and nutrients which promotes/supports the growth of disease causing microorganisms. Grey water from the kitchen is classed as dark grey water (Penn et al. 2012; Birks and Hills 2007). Due to the high contaminant loading in kitchen grey water, it requires a more intensive treatment method compared to bathroom and laundry grey water, and may not be suitable for reuse in most type of grey water recycling systems.

2.1.2 Composition of Contaminants in Grey Water (Quality)

The composition of grey water depends on various factors such as the nature of household and personal care products used, the activities and habits of the residents, the source of the grey water and frequency of use (Prathapar et al. 2005; Al-Jayyousi 2003; Jefferson et al. 2000). Grey water is often characterised in terms of its physical, chemical (organic and inorganic) and biological composition (Morel & Diener 2006).

The main physical characteristic of grey water is its total solids, composed of dissolved, suspended and settle-able solids. The major sources of total solids are from the kitchen sink and dishwasher. These include food particles from the kitchen sink and hair, lint, soil particles and faeces from the washing machine (Eriksson et al. 2002). Levels of total solids that are too high or too low can have an adverse effect on the treatment efficiency of grey water treatment

processes such as disinfection and filtration. Total solids also affect the turbidity (clarity) of the grey water and can lead to the development of anaerobic conditions due to depletion of oxygen. Anaerobic decomposition of organic matter results in the generation of odorous gases such as hydrogen sulphide and ammonia (Tchobanoglous et al. 2003). Suspended solids carry a significant proportion of organic matter and thus contribute to the majority of the organic load in grey water. Table 2.1 shows grey water generated from the kitchen sink has the highest concentration of total suspended solids (TSS) ranging between 227 and 720 mg/l whilst bathroom grey water consist of a much lower TSS concentration of between 54-200 mg/l.

Organic contaminants in grey water are normally composed of a combination of proteins, carbohydrates, oil, fats and greases. Organic contaminants can be sourced from soaps, conditioners, shampoos, perfumes/fragrances, hair dye, household cleaning products, food waste and detergents. The primary contributor of organic contaminants, including oil and grease, are grey water sourced from kitchen sinks and washing machine due to the high content of food waste (Table 2.1) (Almeida 1999). The analysis that can be used to measure levels of organic material and thus the efficiency of treatment process includes biological oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC) (Eriksson et al. 2002). BOD is a measure of the dissolved oxygen used by microorganisms to biologically oxidise the organic matter in the water. One of the disadvantages of the BOD test is that it only measures biodegradable organics. Another disadvantage is that the actual period required for exhaustion of soluble organic matter has not been validated. This reduces the usefulness of the test results (Tchobanoglous et al. 2003). The COD test is used to measure the amount of oxygen required to chemically oxidise the organic matter in water. The resulting value is higher than the BOD value because more organic compounds and some inorganic compounds are oxidised by the chemicals in the test than are oxidised in the BOD test (Tchobanoglous et al. 2003). The TOC test is used to determine the amount of organic carbon present in the water. With the TOC test, all organic and inorganic compounds are oxidised using electrochemistry which means the resulting value would be higher than that obtained either from the BOD or COD test methods. The TOC test is often recommended to validate the BOD test; providing a valid relationship between the two can be established.

Inorganic constituents in grey water include metals, gases and nutrients. Nitrogen in the form of ammonia, nitrate, nitrite and total Kjeldahl nitrogen and phosphorous are nutrients for the biological development of all major micro-organisms in the grey water. These nutrients can also cause significant problems in the environment when discharged into the ecosystem due to

rapid oxygen depletion. Gasses such as methane, ammonia and hydrogen sulphide are developed as a result of anaerobic decomposition of organic matter present in grey water. These gases give off unpleasant odour and are of concern to public health and safety. Very small traces of metals such as cadmium, cobalt, lead, selenium and cobalt can also be found in grey water, these presumably comes predominantly from components of the plumbing system (Tchobanoglous et al. 2003). Nitrogen and phosphorous compounds are found in faecal contaminants and the main sources of these are from washing machines and dishwashers (Table 2.1). Information on the origins of all metals in grey water is limited, although some metals such as cobalt, selenium and molybdenum are sources from food and can be shed through faeces. Some metals may also be brought about as a result of water softeners used in homes. Chloride is another inorganic constituent present in grey water and is sourced primarily through the use of household cleaning products, it is also present in water softeners and in potable water.

Control of biological contaminant is of fundamental importance in the limitation of water borne disease caused by pathogens. Pathogenic organisms can be excreted by animals and humans who are carriers of a particular infectious disease. The class of pathogenic organism that can be found in grey water are bacteria, protozoa, helminths and viruses. Bacteria colonize in the human intestinal tract, one of the most common pathogenic bacteria found in domestic wastewater is *Salmonella* and in some occasion *Clostridium* (Tchobanoglous et al. 2003). All these forms of pathogenic organisms can be sourced from human and animal faeces as well as from soil and insects. The warm temperature often found in grey water is an ideal condition for these organisms to grow. The numbers of pathogenic organisms present in grey water are usually few and it can be quite a challenge to isolate and identify them. For this reason, micro-organisms which are more numerous and are easier to test for are typically used as indicator organisms for the target pathogens. The organisms that have been used as indicators especially for faecal contamination are E.coli, total coliform (TC), faecal coliform (FC), Klebsiella, faecal streptococci, Enterococci, Clostridium perfringens, Pseudomonas aeruginosa and A. hydrophila.

Table 2.1 - Characteristic of grey water compiled from data obtained from numerous literature (Sources; Siegrist et al 1976; Christova-Boal et al. 1996; Surendran and Wheatley 1998; Almeida et al. 1999; Nolde 2000)

Parameters	Unit	Shower	Bath	Wash basin	Kitchen sink	Washing machines	Dishwasher
Physical							
Volume	l/use	32-95	32-95	1.9-7.9	11.6-27	28-151	22.4
pH	-	6.4-8.1	6.4-8.2	8.1	7.8	8.1-10	7.8
EC	µS/cm	82-250	-	-	-	-	-
Turbidity	NTU	60-240	-	102	-	108	148
TSS	mg/l	119-200	54	181	222-720	65-280	15-440
Chemical							
COD	mg/l	280-501	210	95-433	138-1400	700-725	-
BOD	mg/l	43-216	-	252	530-890	472	390
PO_4-*P*	mg/l	1-5.3	-	13.3-50	10.0-74	23-200	32
NH_3	mg/l	01-Feb	-	0.3-1.15	0.3-6	0-11	4.5
MBAS	mg/l	61	15	3.3	59	42	11.1
Biological							
Total Coliform (TC)	CFU	$10\text{-}2.4x10^7$	-	-	$>2.4x10^8$	$200\text{-}7x10^5$	-

2.1.3 Daily Household Grey Water Discharge (Quantity)

The volume of grey water generated by an individual will depend on the efficiency of the device used and the water usage practices of the individual. The typical volume of grey water generated varies from country to country and ranges between 90-400 litres per person per day in developed countries and around 20-30 litres per person per day in a developing country (Cosgrove and Rijsberman 2014; Morel and Diener 2006). Various studies have been conducted to determine the volume of grey water generated at various sources per day. A summary of these studies taken from published literature is detailed in Figure 2.1 (Mourad et al. 2011). It can be seen that on a daily basis, the bathroom is the major contributor of grey water, producing on average 60 litres of water per person per day which equates to 50% of total grey water discharge.

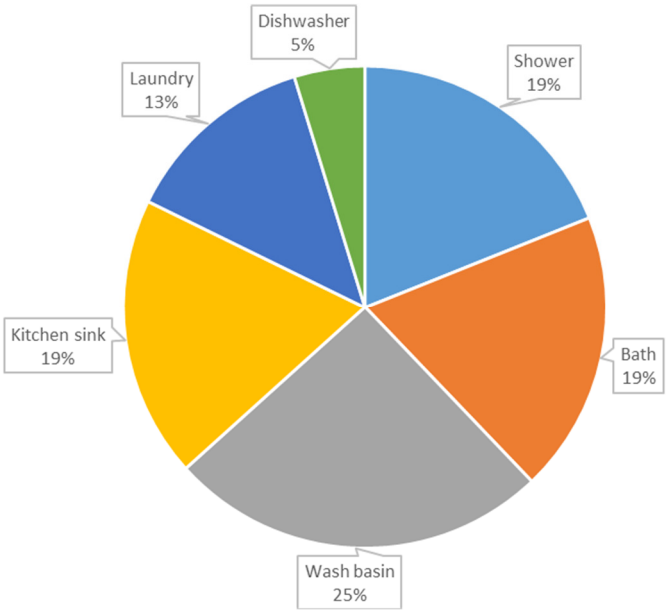
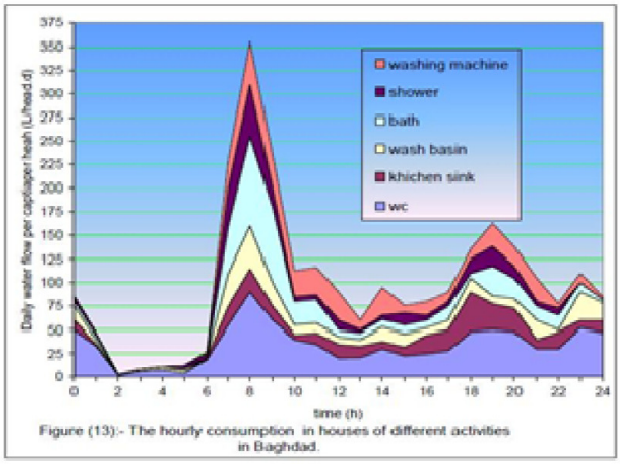


Figure 2.1 - Daily water consumption for various household activities in litres per person per day (l/p/d) (Mourad et al. 2011)

Studies conducted in various countries to determine the loading rate of grey water over 24 hour is illustrated in Figure 2.2. The figure demonstrates that the majority of grey water produced per day was generated between the hours of 6 am to 10 am and 5 pm to 10 pm which corresponds to the time period where residents are at home from work or school (Abbood et al. 2013; Eriksson et al. 2009; University of Wisconsin 1978). A reduction in grey water discharge rate results in a more concentrated grey water solution with high contaminant loading (Eriksson et al. 2009).

(a)



(b)

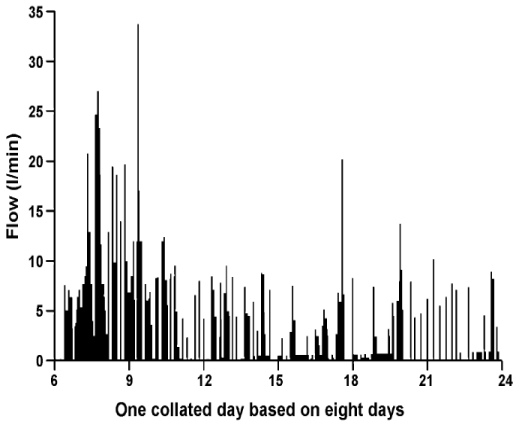


Figure 2.2 - Hourly grey water variability obtained from literature (a) Abbood et al. 2013; (b) Eriksson et al. 2009

2.2 Grey Water Recycling

2.2.1 Relevance and Impact

Grey water reuse on a large scale is a fairly new concept. It is known however that on a smaller scale, ancient Romans made allowances in their water supply infrastructure for re-using domestic wastewater for non-potable use (Monteleone et al. 2007). Whilst the importance of good quality drinking water has been recognised since ancient times, the importance of proper sanitisation for the protection of public health was not fully understood by urban population until the late 19th century (Vuorinen et al. 2007).

For centuries, domestic wastewater in most parts of the world was disposed of in the streets and around populated areas without consideration being given to its effect (Lofrano and Brown 2010). As a result, there were serious impacts on public health and the environment, which is evident from the numerous epidemics that occurred worldwide. Such epidemics are still prevalent in certain parts of the world such as Haiti, Southern Asia and some parts of Africa (Wickstead 2011). It is evident that grey water reuse from the 20th century is only a rediscovery of ancient urban practices, brought up to date by advancement in the treatment technologies used.

The whole concept behind grey water recycling is that water that has already been used once for a domestic activity, rather than being returned to the sewer, is reused for another domestic or agricultural application that does not require the use of potable water (Jamrah et al. 2006; Al-Jayyousi 2003; Faruqui amd Al-Jayyousi 2002; Eriksson et al. 2002; Nolde 2000). Hence, grey water recycling has the potential to extend existing water supply by reducing demand for potable water, lower the need for new water supply infrastructure (Atwater 1998).

The source of the grey water and the level of treatment determine the reuse constraints. For instance, grey water from bathrooms is less contaminated than laundry grey water. Grey water from a commercial/business bathroom can be less contaminated than that from a residential bathroom. Hence for a similar reuse purpose, grey water sourced from a residential bathroom would require a more intensive treatment than grey water sourced from a commercial bathroom.

In some rural parts of the world, it is common practice to reuse grey water drawn from bathing and laundry without any treatment. However, treatment is necessary in most cases to prevent health risks and environmental effects (Dixon et al. 1999, Diaper et al. 2001).

Irrigation is the most common reuse application of recycled grey water. Untreated grey water can only be used for subsurface irrigation or applied directly to the soil rather than through a sprinkler. This is to reduce the likelihood of untreated grey water runoff into rivers as well as direct contact with the public. Grey water containing bleach and those sourced from the kitchen, dishwasher and laundry cannot be used for irrigation due to the presence of substances (such as grease, fats, oil and fabric softener) which may have detrimental effects on the health of the plants. Grey water which has been appropriately treated and/or disinfected can be used for toilet flushing, and can also be reused for some applications involving human contact such as household cleaning, car washing and laundry. Recycled grey water used in applications involving human contact must however be treated to a higher standard in order to satisfy government legislations.

Although grey water reuse offers possible solutions to water shortage now and in the future, it also presents many health and environmental concerns. The main public health risks associated with grey water reuse are inhalation of aerosols from untreated grey water, direct physical contact with grey water as well as ingestion of food that has come into contact with grey water especially during irrigation. The level of risks can be controlled by treating the grey water to reduce the amount of disease causing microorganism to a safe level, followed by disinfection as well as by managing the methods of reuse application and public accessibility. The risks associated with grey water reuse have long been recognised and measures have been put in place by regulatory bodies to prevent these risks.

Research has been conducted over the past decade to evaluate the potential water savings from grey water recycling. A study undertaken by Ghisi and Ferreira (2007) to compare the economic benefit of a grey water and rainwater recycling system demonstrated that the grey water recycling system is more cost effective with a payback period of less than 5 years and total percentage potable water savings of 28.7% to 34.8%.

The majority of the study conducted found that the savings generated from using a grey water recycling system outweighs the cost incurred (Mandal et al. 2011; Mourad et al. 2011; Campisano and Modica 2010; Godfrey et al. 2009). Another interesting finding is that the economic benefit of a grey water recycling system increases with the number of users (Mourad et al. 2011; Friedler and Hadari 2006). For example, Friedler and Hadari (2006) reported that their treatment technology became more economically feasible when the sample building size increased.

2.2.2 Grey Water Legislation and Treatment Requirements

The issue with treating grey water is whether the quality of the water after treatment is suitable for a particular reuse purpose. Until recently, grey water treatment and reuse applications have not been given much consideration by government and regulatory bodies worldwide. As a result, grey water reuse has often been carried out without the requirements of a regulatory framework. International interest in water conservation and the widespread applications of reused grey water has resulted in recent surges in the development of standards and regulatory codes of practice specifically for grey water treatment and reuse applications. However, regulatory bodies in some parts of the world are either in the process of developing reuse standards or have still not put one in place. This section reviews grey water reuse codes of practice in various parts of the world highlighting treated grey water quality requirements. Information provided in these standards are simplistic, relying on users to actively manage their system. The quality requirements are often divided into restricted (spray) and unrestricted (non-spray) reuse applications. A summary of the treated grey water quality requirements for different parts of the world is provided in Table 2.2.

2.2.2.1 Australia

The seven year drought in Australia in the late 1990s and recent water shortage in many parts of Australia has served to focus public attention on the need for a more sustainable water use (Australian Government Department of the Environment, 2010). This may be one of the reasons why Australia when compared to some parts of the world, seem to be ahead in the move to implement grey water reuse as one of the key methods of water conservation.

In June 2004, the ACT (Australia Capital Territory) Government released the *"Think water, act water"* strategy with the aim of addressing sustainable management of water resources. This strategy aims to achieve 25% reduction of mains water use by 2023. Furthermore, the ACT Government also aim to increase the use of reclaimed water to 30% by 2015 in Australia (Act Government Australia, 2008; Geary *et al*. 2005). Reusing grey water is endorsed as a way of contributing to the achievement of this reuse target.

Australia does not have a national code of practice which regulates grey water reuse practices, States and Territories are given responsibility for regulating such practices. For example, residents in New South Wales interested in installing grey water systems require approval from local government authorities. This is fairly similar in Victoria, where residents must contact local authorities and put in an application. It is an offence for residents in Western Australia to commence installation of a grey water device without government approval, whilst in Canberra the nation's capital, residents do not require council permission but are instead required to have the plumbing inspected after installation.

The legislation covering grey water reuse is covered in Queensland by the Plumbing Act (Office of the Queensland Parliamentary Counsel, 2011), in Victoria by the Environment Protection Act and in New South Wales by the Local Government Act (Tufvesson, 2009). Other documents which set minimum requirements for grey water reuse in urban and rural cities in Australia are available for properties in Canberra and Western Australia.

The Western Australian code of practice suggests three methods of grey water reuse; bucketing, grey water diversion device and grey water treatment systems. Each reuse methods have different permitted end use and approval requirement (Government of Western Australia, 2010).

The treated water quality requirement in Western Australia is less than 20 mg/l BOD and less than 30 mg/l suspended solids. Reuse applications such as toilet flushing, irrigation and laundry which are likely to result in spraying require more intensive treatment. The treated water quality requirement for this reuse purpose is less than 10 mg/l BOD, less than 10 mg/l suspended solids and less than 1cfu/100 ml total coliform (Table 7.1).

The treated grey water quality requirement set out in reuse guidelines for properties in Canberra are 20 mg/l BOD and 30 mg/l suspended solids for restricted applications such as sub-surface

irrigation; 20 mg/l BOD, 30 mg/l suspended solids and 10 cfu thermo-tolerant coliforms/100 ml for unrestricted applications (Australian Capital Territory, 2007).

2.2.2.2 United States of America

The United States of America is another leader in grey water reuse applications and technologies. One of the reasons for this may be due to the fact that about 60% of homes in the USA are not connected to a sewerage system (Jeppesen 1994). Another reason may be because some regions such as Texas, Florida, Southern California and Arizona are extremely dry and are experiencing rapid population growth. These areas have especially been investigating alternative and sustainable water sources.

In August 1989, Santa Barbara, California was one of the first to legalise the reuse of grey water. The city of Santa Barbara published the first grey water reuse guidelines in the US in May 1990, which is limited to single family residential use (Oasis design 2009). The document was later revised in 1997 to allow for multi-family use.

In the late 1980s, Florida also legalised grey water reuse. The total reuse capacity of Florida's domestic wastewater treatment facilities increased by 281 per cent from 1986 to 2001 (Canada Mortgage and Housing Corporation 2002).

In January 2001 Arizona issued a one blanket permit for every grey water system in the state, this approach was also adopted by New Mexico in March 2003 (Oasis design 2009). Under Arizona regulations, systems producing less than 1,515 litres a day must meet a list of best management practices and are covered by the general permit.

Regulatory codes of practice or guidelines have been developed in Nevada, New Jersey, New Mexico, Arizona, California, Florida, Georgia, Colorado, Massachusetts, Hawaii, Utah, Texas, Ohio, Wyoming, North Carolina, Washington and Oregon, these guidelines strongly recommends water reuse as a method of water conservation. Apart from New Mexico, Georgia, Ohio and Wyoming, all the other states specify guidelines and regulations for reuse purposes other than irrigation (Environmental Protection Agency 2004).

2.2.2.3 Europe

In the European Union (EU), there are also no standards specifically addressing grey water reuse. The Urban Wastewater Treatment Directive however regulates urban wastewater treatment in the EU. The document sets out obligations for treatment and defines the quality of effluents released to the environment (European Commission 2011).

Codes of practice for treatment and reuse of grey water have been set out in the UK. The BS8524-2010 was published by the British Standards Institution (BSI) in June 2010 and provides guidance and recommendations for the design, installation, testing, modification and maintenance of grey water reuse (British Standards Institution, 2010). The document only covers grey water systems utilising water sourced from the bathroom to provide non-potable water reuse in the UK. It does not necessarily condemn use of grey water from other domestic sources. The specified treated water quality requirement is 10 total coliform/100 ml and less than 10 NTU turbidity concentrations for unrestricted applications, whilst for restricted application the quality requirement is 1000 total coliform/100 ml and turbidity of less than 10 NTU (Table 2.2). The guideline does not however, specify treatment requirements for organics or oxygen demand in the treated grey water.

In Europe, Germany is at the forefront in encouraging widespread reuse of reclaimed water. In 1995 the German Berliner Senate Office for Construction and Housing published the first guidelines for service water reuse. As detailed in Table 2.2, parameters were defined for total coliforms less than 100 m/l, faecal coliforms less than 10 m/l and BOD less than 5 mg/l (Nolde, 2000). For other European countries guidelines for water reuse either do not exist or are in the process of being put in place. Some European countries interested in water reuse often aim for treated water quality outlined in the *EU – Guidelines for Bathing Waters*. For instance, the treated water quality for the first official grey water reuse project started in Berlin, Germany in 1989 was in accordance with the *EU – Guidelines for Bathing Waters* (Nolde, 2005).

2.2.2.4 Rest of the World

Legislation for grey water recycling in Asia are covered in documents provided by the World Health Organisation (WHO). Since the Meeting of Experts in 1971, WHO came to the realisation that wastewater which was considered unacceptable for public health, is being used for irrigation in many regions without authoritative recommendations or guidance. The World Health Organisation (WHO) then went on to publish its first wastewater reuse guidelines using the guidelines set in California USA as a benchmark (World Health Organisation, 1973). The document aims to facilitate rational use of wastewater for agricultural purpose; it also provided guidance on how to ensure public health and the environment is protected.

A thorough review of new research and information led to the conclusion that the standards adopted in California, USA were unjustifiably restrictive. As a result, the document was reviewed and a second edition was published in 1989 (World Health Organisation, 1989). In the revised document, considerable importance was attached to wastewater quality control and testing was suggested for: protozoan cysts and eggs of helminthic parasites, faecal coliforms, viruses; *Clostridium* species, chemicals and traces of organics.

The third edition of the document was published in 2006. It is based on new health evidence expanded to better reach key target audiences and to take into account contemporary thinking on risk management (World Health Organisation, 2006). The third edition only highlights the microbiological requirements and the maximum tolerable soil concentrations of various toxic chemicals (based on human health protection), no reference is made on the physical and organic quality level requirements. According to the document, the amount of E.coli and Helminth eggs in the treated grey water used should be less than 10^3/100 ml and 1/1 l respectively for unrestrictive irrigation and 10^5/100 ml and 1/1 l respectively for restrictive irrigation. It should be noted that the guidelines provided in the documents are limited to wastewater reuse for agricultural and aquaculture purposes only.

Table 2.2 - *Treated grey water quality standards across the world compiled from various literature (Source; Li et al. 2009; Asano 2007; Surendran and Wheatley 1998)*

	Reuse applications	pH	COD (mg/l)	BOD (mg/l)	Total Coliform (CFU/100 ml)	Turbidity (NTU)	TSS (mg/l)	TDS (mg/l)	Chlorine (mg/l)
Bathing water standards	Unrestricted	6 to 9	-	-	500	-	-	-	-
UK	Unrestricted	5 to 9.5	-	-	10	< 10	-	-	< 2
	Restricted	5 to 9.5	-	-	1000	< 10	-	-	< 2
Germany	Toilet flushing	-	7.2	5	100	-	-	-	-
USA	Unrestricted	6 to 9	14.3	10	-	< 2	-	-	1
	Restricted	6 to 9	43	30	-	-	30	-	1
Australia	Unrestricted	6.5 to 8.5	-	-	10	< 2	-	-	1
	Restricted	6.5 to 8.5	-	-	1000	< 2	-	-	1
Australia (Canberra)	Unrestricted	-	28.6	20	10	-	30	-	-
	Restricted	-	28.6	20	-	-	30	-	-
Western Australia	Unrestricted	-	28.6	20	10	-	30	-	-
China	Restricted	6 to 9	14.3	10	-	< 5	-	< 1500	> 0.2
	Unrestricted	6 to 9	8.6	6	-	< 5	-	> 1000	> 0.2
Japan	Toilet flushing	5.8 to 8.6	28.6	20	1000	Not unpleasant	-	-	Retained
	Irrigation	5.8 to 8.6	28.6	20	50	Not unpleasant	-	-	≥ 0.4

2.3 Graphite Intercalation Compounds (GICs)

2.3.1 Introduction to GICs

Graphite is a crystalline allotropic form of carbon with moderate electrical conductivity. The graphite structure is made up of succession of graphene layers parallel to the basal plane of hexagonal lattice of carbon atoms as illustrated in Figure 8.1 (Noel and Santhanam 1998). The distance between the carbons (C-C) in the hexagonal lattice is 1.42 Å, compared to a distance of 3.35 Å between the graphene layers (Charlier et al. 1989; Franklin 1951). The graphene layers are held in place by Van der Waal's force which is significantly weaker than the carbon-carbon bonds within the hexagonally linked layers held together by strong covalent bonds (Ubbelohde and Lewis 1960).

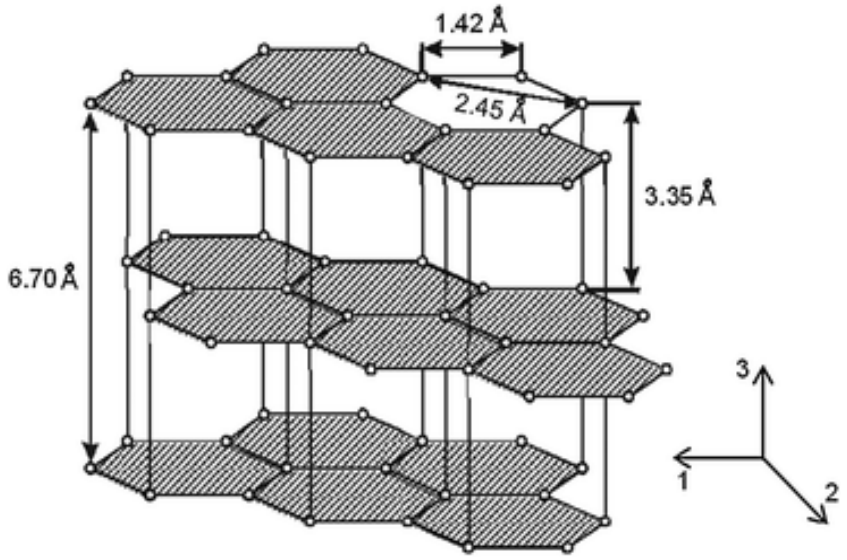


Figure 2.3 - Structure of graphite (Śliwińska-Bartkowiak et al. 2012)

In its ground state, carbon atom contains six electrons in the $1s^2 2s^2 2p^2$ configuration (Figure 2.3). The electrons located at the outer 2p orbital (the valence electrons) are the only once available for bonding to other atoms. The valence electrons can be easily removed when an electric potential, high enough to offset the binding energy of the electron to the carbon atom is applied.

In going from ground state to graphite structure three out of four electrons in the 2s and 2p orbital are redistributed into hybrid $2sp^2$ orbitals (Figure 2.4). The fourth electron fills the p orbital which does not take part in the $2sp^2$ hybrid used in covalently bonding to three other carbon atoms in a plane. The delocalised un-hybridised 2p electron (pi (л) orbital) is oriented perpendicular to the plane of the hybridised sp^2 orbitals (sigma (σ) orbital). Each carbon in the hexagonal lattice contributes a delocalised л electron, which are free to move throughout the planes of carbon atoms and thus gives graphite its electrical conductivity properties (Brandt 2012; Pierson 1994; Charlier et al. 1989; Zaleski 1985).

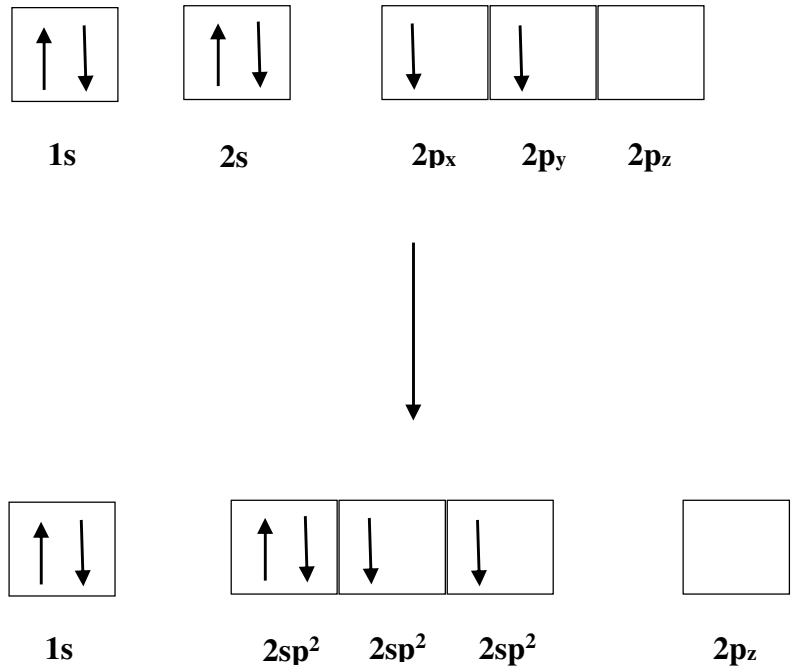


Figure 2.4 - Schematic of the electronic structure of carbon atom in its ground state and the sp2 hybridisation of carbon orbital (Pierson 1994)

There are two main ways in which compounds can be derived from graphite. One way is by species forming covalent two-electron bonds with the carbon atoms. Another method is by charge transfer to and from the graphene sheets. Covalent bonds are typically formed when graphite reacts with elements or groups of high electronegativity. For instance, reaction with oxygen or hydroxyl groups generates graphite oxide. In this case, the carbon sheets lose their planarity and the disruption of the π-electron system results in a drastic decrease in the electrical conductivity of the host graphite (Dreyer et al. 2010; Boehm et al 1994a; Zaleski 1985; Rüdorff et al. 1963). The charge transfer method on the other hand occurs through the insertion (intercalation) of the guest species (intercalant) between the host graphite layers. The weak Van

der Waals forces between the graphene layer accounts for the high anisotropic properties of graphite which makes it possible for species to be inserted between graphene layers of graphite (Ubbelohde and Lewis 1960). During this reaction, the graphene sheet of the host graphite retains their planer structure, the graphene layers are merely split slightly whilst the reacting species forms a monolayer between layers of graphene. When the host graphite and the guest species interact by charge transfer, the distance between graphene sheets increases, which enables delocalised electrons to move more freely. This increase in distance between the graphene layers depends on the intercalant used and ranges from 5.3 Å in a potassium-GIC (Belash et al. 1990) to around 12.03 Å in a DMSO (Dimethylsulphoxide)-solvated magnesium chloride-GIC (Meada et al. 1988).

Graphite can react with a range of intercalant to form graphite intercalated compound with different properties and several have already been manufactured (Belash et al. 1990). Two forms of GIC, namely acceptor and donor type GIC, can be generated depending on the method of electron transfer between the intercalant and the host graphite (Özmen-Monkul and Lerner 2010). An acceptor type GIC is manufactured by oxidisation of the graphite to accept anionic intercalates and requires a strong oxidant (Boehm 1994a; Zaleski 1985). Whilst for donor type GIC, graphite is reduced to accept cationic intercalates using strong reducing agent (Boehm 1994a). The distinct property of graphite compared to other anisotropic type system which can also react with intercalants is that GIC has a constant layer of graphene layer between two monolayer of intercalant (Chen et al. 2003). This regular ordering of graphene and intercalants is called staging (Conte 1983). Stage 1 indicates that a monolayer of intercalant is present between each graphene sheets whilst a stage 2 indicates the presence of intercalants monolayer between two graphene layers (Figure 2.5). Control of the condition of the intercalation reaction can control the stage number of the GIC.

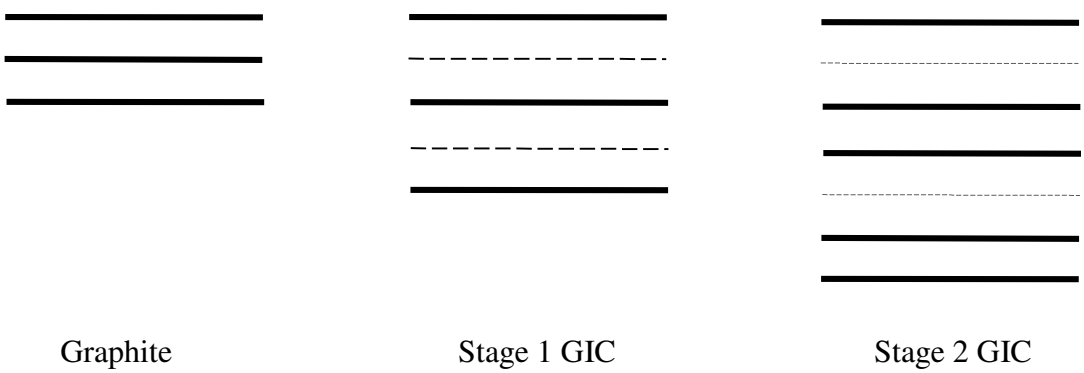


Figure 2.5 - Schematic representation of staging in GIC

2.3.2 Synthesis of GICs

Graphite intercalation compounds can be prepared using several methods, the most common techniques are vapour phase reaction, liquid phase reaction and electrochemical reaction (Charlier 1989). During vapour phase reaction, the host graphite is placed with the intercalant in a reaction chamber (Figure 2.6). The reaction chamber is separated into two zones, the two zone (one holding the host graphite and the other zone holding the intercalant) are maintained at different temperatures T_g and T_i respectively (Twumasi 2002; Charlier 1989).

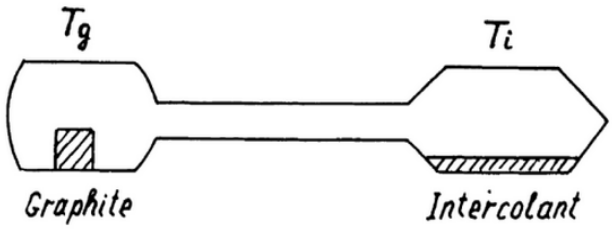


Figure 2.6 - Schematic of the two zone chamber used for vapour phase intercalation technique. Graphite is maintained at T_g and the intercalant at T_i (Charlier 1989)

In order to maintain the intercalation reaction process, the temperature of the graphite zone must be higher than the intercalant zone. A displacement in the temperature in each zone results in precipitation of intercalant on the surface of the host graphite which impedes intercalation.

During the intercalation reaction using the vapour phase technique, the intercalant zone temperature is kept constant whilst the graphite zone temperature is varied. Once the operating temperature difference has been obtained, the vapour of the intercalant passes through from the intercalant zone to the host graphite zone. The stage index of the intercalated compound can be controlled be selecting the temperature difference between the two zones. Since the temperature at the intercalant zone is kept constant during reaction, the stage number of the intercalated compound is determined by varying the temperature at the host graphite zone. Compared to the liquid phase and electrochemical interaction technique, the vapour phase technique is the most commonly used due to its simplicity. However, the vapour phase technique is applicable only to highly volatile intercalants. This is because the temperature at which the intercalation zone is set depends on the vapour pressure of the intercalant, and intercalation cannot occur below the vapour pressure.

With the liquid phase intercalation technique, the intercalation process occurs when the host graphite is added to a solution of the intercalant and boiled under reflux. The reflux temperature can be varied over a wide range up to the boiling point of the solution (Brandt et al. 2012). A dry inert solvent is used and the temperature of the reaction is carefully controlled to prevent the solvent reacting with the intercalant (Twumasi 2002; Maeda et al. 1985). One advantage of the liquid phase process is that it enables a more homogeneous product as well as a large quantity of product (Twumasi 2002). Electrochemical intercalation process is often used for strong acid intercalants. The process uses two electrodes which are placed in an acidic solution. The host graphite is either placed with the anode electrode for oxidation to give C^+ lattices which can hold anionic intercalants or with the cathode electrode for reduction to give C^- lattices which can hold cationic intercalants. In synthesis, the voltage is applied across the electrodes and the stage index is determined by selecting the operating voltage (Noel and Santhanam 1998; Inagaki et al. 1990).

When GICs are heated past a critical temperature, usually above 100°C, a large expansion perpendicular to the graphene layer occurs. The high temperature results in changes in the volume of the intercalant between the graphene layers which further weakens the Van der Waals force holding the graphene layers together. This leads to the expanded GIC known as exfoliated graphite intercalation compound. Exfoliated GICs are characterised by their lower density, loss in mass and increased surface area (Chung 1987).

2.3.3 Classification of GICs

It is possible to manufacture a wide range of GICs by using different intercalant. Common intercalants used to produce donor type intercalation compound are compounds of alkali metals such as K, Rb, Cs and Li (Maeda et al. 1988). On the other hand, acceptor type intercalation compounds are generated using Lewis acid intercalant such as bromide, fluoride and strong Bronsted acids such as H_2SO_4 and HNO_3 (Emerya et al. 2009; Chung 2002; Maeda et al. 1985). GICs which are intercalated with one intercalant are known as binary intercalation compound (Chartlier et al. 1989) an example of a binary intercalation compound is graphite bi-sulphate and graphite perchlorate. On the other hand, intercalation of host graphite with two intercalant results in ternary type intercalation compound (Emerya et al. 2009). Compared to all other intercalant, the acidic form of intercalants provides GICs with unique electrical conductivity properties on the basal plane of the GICs. The electrical conductivity at the basal plane can be

controlled by varying the strength of the acidic intercalant. At a relatively high acid concentration, the density of delocalised holes on the graphite increases which results in increased electrical conductivity of the resulting GIC (Fischer 1980).

2.3.4 Application of GICs

Due to their high electrical conductivity, electrochemical activity and thermal insulation, GIC has received vast interest for various uses. The insulating properties of GICs have led to their use as thermoelectric materials for thermal energy storage and in power sources such as electrodes and batteries. For instance, potassium and lithium intercalated graphite compounds are superconducting GIC which have been used in batteries (Wang et al. 2014; Whittingham et al. 2000). Nickel and potassium intercalated graphite have also proved effective for use as catalysts (Sirokman et al. 1990; Bolz 1977), the high electrical and low thermal conductivity properties of GICs has been very well exploited for industrial use (Enoki et al. 2003).

The majority of literature available on the use of GIC as an adsorbent material is limited. The literature that has so far been published was as a result of work done using Nyex™ adsorbent. There has however been some information on the use of graphite oxide as an adsorbent.

Graphite oxide is a similar compound to GIC but is more highly oxidised and rich in functional groups containing oxygen (Jia et al. 2011). Graphite oxide was successfully used by Hartono et al. (2009) to adsorb humic acid from an aqueous solution. Hartono et al. (2009) reported an adsorption capacity of 190 mg/g which is much higher than that of activated carbon (Daifullah et al. 2004). The high adsorption capacity of graphite oxide is brought about as a result of the oxygen functional group present in the graphene structure. However, in synthesis of graphite oxide, the graphene layers of the host graphite lose planarity which results in a decrease in the electrical conductivity of the resulting graphite oxide (Boehm 1994b). Olanipekun et al. (2014) also reported successful adsorption of lead from wastewater onto graphite oxide. Graphite oxide intercalated with n-hexadecylamine was used to adsorb pyrene from a water-ethanol solution. An adsorption capacity of 28.5 mg/g was reported with pyrene adsorbed both on the external graphite surface and between graphene layers (Matsuo et al. 2003).

Exfoliation of GIC produces a light weight material with a large surface area. The use of exfoliated GIC has been investigated for the adsorption and recovery of heavy oils (Vieira et

al. 2006; Toyoda and Inagaki 2000) and for the adsorption of organic pollutants from wastewater (Goshadrou and Moheb 2011; Skowroński and Krawczyk 2004).

Graphene is a single layer of graphite packed in a regular sp2 bonded atomic form. The unique properties of graphene was first explored by Brodie (1859) who reported on the lamella structure of graphene. Graphene can be isolated from graphite by various means and if prepared properly is very strong, flexible and is an excellent conductor of heat and electricity. These fascinating characteristics of graphene material mean it has several potential applications such as solar cells, electric circuits and for flexible screen displays (Kusmartsev et al.2014). Gupta et al. (2012) reported the use of a graphene material formulated from sugar for the adsorption of rhodamine and chloropyrifos. Results showed high adsorption capacity which like the graphene oxide was higher than that of activated carbon. However, in order to use graphene for wastewater treatment, the material has to be anchored to a reliable substrate to overcome engineering issues such has pressure drop and solid-liquid separation.

2.3.5 Development of Nyex™ Adsorbent by Intercalation Method

The form of GIC used in this project is the graphite bi-sulphate form manufactured from flake graphite. A strong oxidising medium is used in the presence of concentrated sulphuric acid intercalant to produce a GIC with the formula $C_2 4HSO_4 y H_2SO_4$, where y can vary between 2 and 2.5 (Excell et al. 1989). Due to environmental and health and safety concern of the manufacturing process, which uses large quantities of sulphuric acid, the graphite bi-sulphate GIC was manufactured by Nykin Development and is supplied under the trade name of Nyex™.

2.3.6 Characteristics of Nyex™ Adsorbent

Nyex™ adsorbent is a novel, non-porous and highly-conducting graphite based material. Mercury porosimetry showed there were no internal pores in the adsorbent material, thus proving the non-porous structure of the Nyex™ adsorbent. The non-porous nature of the Nyex™ results in lower adsorption capacity of 2 mg g^{-1} (5 mg l^{-1} of crystal violet dye) compared to its carbon based alternatives such as activated carbon, which has an adsorption capacity of 40.6 mg g-1 (1.9 mg l^{-1} of crystal violet dye) (Brown et al. 2004b). Nyex™ was selected because it has no internal surface area, this characteristic was thought likely to result in quick adsorption and electrochemical regeneration as intra-particular diffusion is eliminated. The higher

electrochemical conductivity of Nyex™ also enables simple and quick electrochemical regeneration which is an extremely important part of the Arvia™ process.

The flaked GIC adsorbent has a mean particle diameter of 448 µm and surface area of 3.44 m^2. The adsorbent content is comprised mostly of carbon with carbon content of over 95%, all other material which is not carbon forms the impurities or ash upon oxidation. The non-porous nature of the adsorbent means it has a fairly high particle density of 2.2 g/cm^3 with packed bed electrical conductivity of 0.8 S/cm. The particle size of Nyex™ was determined using sieve analysis. The Nyex™ material was found to have mean particle size diameter of 450 µm with particle size ranging from 100 to 1000 µm (Figure 2.7).

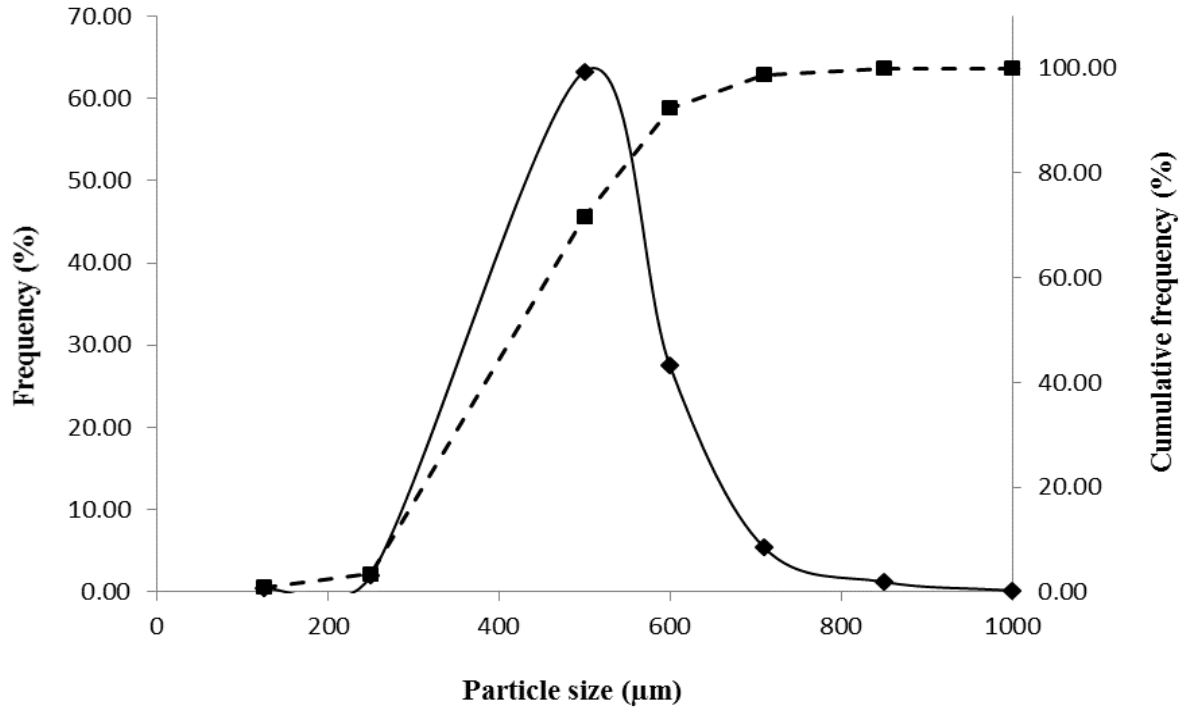


Figure 2.7 - Particle size distribution of Nyex™ adsorbent

Nyex™ surface structure is made up of flat layer basal planes held together by Van der Waal forces and perpendicular to this are fragmented/dislocated edge planes. The basal planes are made up of hexagonal lattice of carbon atoms and consist mainly of non-polar characteristics. The fragmented edge planes consist of chemisorbed surface functional groups which are known to influence the adsorption capacity (Hartono et al. 2009; Goyal and Bansal 2005). The functional groups on the edge planes of Nyex™ are acidic oxygen containing functional groups, a large proportion of which are phenolic hydroxyl groups with lower concentration of carboxyl and carbonyl groups (Nkrumah-Amoako et al. 2014).

2.4 Adsorption Process

2.4.1 Adsorption Classification

The tendency of a contaminant to be adsorbed by an adsorbent depends on the hydrophobicity/solubility of the contaminant, or the affinity of the contaminant to the adsorbent. This is because the less soluble a contaminant is in water, the easier it will be to remove from water compared to contaminant which is completely soluble in water. Similarly, non-polar contaminants will be more easily removed compared to polar contaminant as polar substances have a greater affinity to water (Von Oepen et al. 1991).

Since adsorption is a surface process, the surface area of the adsorbent is also important. The surface area available for adsorption increases with decrease in the size of the adsorbent particles. Other factors which affect adsorption are electrostatic effects, concentration gradient, molecular size of adsorbate, surface chemistry, pH and steric effects (Do 1998; Vidic et al. 1993; Ruthven 1984).

Adsorption can be classified as either physical adsorption (physisorption) or chemical adsorption (chemisorption) (Faust and Aly 1987). Physical adsorption is due to Van der Waal's attraction forces and can under the correct conditions be easily reversed. Under certain conditions, physisorption can result in multilayer adsorption where molecules already adsorbed in the adsorbed phase attract molecules from the liquid phase. Chemical adsorption relies on a chemical reaction resulting in the formation of chemical bond, unlike physisorption, chemisorption is more difficult to reverse and does not form multilayers. Depending on the adsorbate and the surface of the adsorbent, adsorption can also result in electrostatic interaction due to charged adsorbate forming ionic bond with charges on the surface of adsorbent (Weber et al.1991).

Adsorption can occur at various locations on the adsorbent such as the outer surface or within the pores of the adsorbent. The adsorption process takes place in four major steps as follows (Tchobanoglous et al. 2003) (Figure 2.8):

1. *Bulk solution transport* – the movement of contaminants (adsorbate) from the bulk liquid phase to the surface of the adsorbent. This phase is usually fast and depends on agitation of the solution.

2. *Film diffusion transport* – transport of the contaminant through the fixed liquid film surrounding the adsorbent to the surface of the adsorbent, by diffusion.
3. *Pore transport* (intra-particle diffusion) – transport of the contaminant through the adsorbent pores, typically by molecular diffusion.
4. *Adsorption* – attachment of contaminant on an available adsorption site.

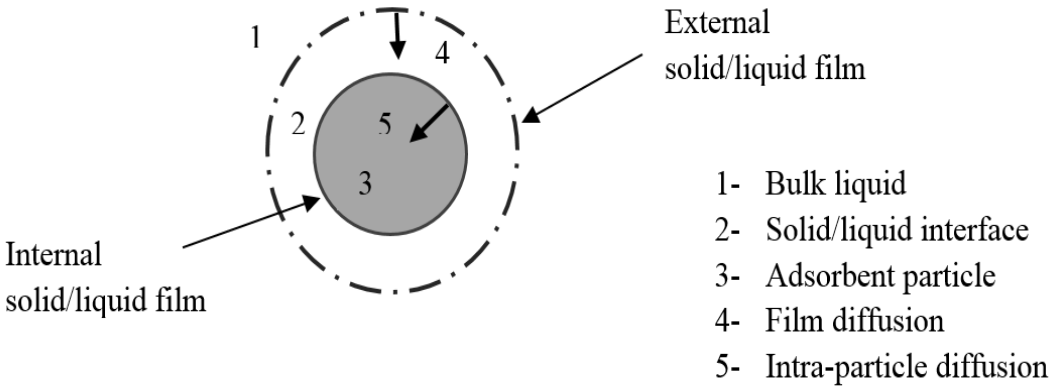


Figure 2.8 - Schematic illustrating the microscopic adsorption steps which occurs around an adsorbent particle.

If physical adsorption is the principal adsorption method, the rate limiting step (the slowest step) is usually step 2 or 3. For non-porous adsorbent, intra-particle diffusion (step 3) is eliminated in the adsorption process which often results in increased adsorption rate and eases recovery of the adsorbent at the expense of reduced adsorption capacity. In contrast, the rate limiting step for chemical reaction is the step 4 due to bond formation between contaminants and adsorbent.

2.4.2 Adsorption in Wastewater Treatment

Adsorption represents a fundamental process in both industrial wastewater treatment and water purification. It has so far proven to be a very effective and economical method for removing organic contaminants even at low concentrations (Nemr et al. 2009; Namasivayam and Kavitha 2002; Cooney 1998; Vidic et al. 1993). A wide range of adsorbent such as activated carbon (Wu et al. 2011; Li et al. 2010; Wang et al. 2005; Malik 2004; Mueller et al. 2003; Kadirvelu et al. 2001; Mohan et al. 2000), zeolites (Ok et al. 2007; Wang et al. 2006; Sarioglu 2005; Perić et al. 2004) and silica (Aguado et al. 2009; Andrzejewska et al. 2007; Al-Ghouti et al. 2003)

are utilised for the removal of organics, inorganics and heavy metal contaminants in varying composition. This results in the reduction of COD, BOD, odour and colour from wastewater which otherwise is fairly resistance to biological degradation and are not effectively removed by other physio-chemical treatment method, such as filtration, coagulation and sedimentation.

Of all the adsorbents used in industrial wastewater treatment and in the majority of research work, activated carbon is employed extensively due to its high affinity to organic compounds even at low concentrations (Dąbrowski 2001). Activated carbon is often used either in its granular or powdered form. For an adsorption process using granular carbon, the water to be treated is either fed from the top of the packed bed and flows downwards (down-flow mode) or is fed under pressure at the bottom of the cell and flows upwards (up-flow mode). Suspended solids present in the wastewater get trapped between the packed bed and are removed by backwashing the bed in order to reduce flow restriction. Alternatively, the bed can be partially fluidised by increasing the up-flow pressure so as to prevent or minimise blockage. If the powdered form or activated carbon is utilised, the activated carbon is added to the wastewater and the slurry is often mixed to encourage mass transfer (Cooney 1998).

Although fairly limited there have been a number of studies undertaken to investigate adsorption of organic contaminants onto Nyex™, and results have shown significant and rapid uptake of organics though with low adsorption capacity due to the low surface area of the adsorbent as a result of its non-porous characteristics (Asghar et al. 2012a; Brown et al. 2004a). Research on the adsorption of inorganic contaminants onto Nyex™ is currently limited, recent studies of the adsorption of ammonia onto Nyex™ showed that Nyex™ was able to adsorb ammonia (Akmez Nabeerasool, Personal communication, November 28, 2013). The solution used in this study contained only ammonium chloride which makes it difficult to compare with adsorption in grey water solution, where ammonia is present with other compounds. There are several reports on the adsorption of inorganics onto other adsorbents such as zeolites, activated carbon and silicate from single component solutions (Ho et al. 2000; Shin et.al. 2004; Englert and Rubio 2005). Unfortunately, reports on the adsorption of organic and inorganic contaminants from multicomponent solutions such as grey water are limited. The work in this thesis would for the first time investigate the adsorption of organic and inorganic contaminant from a multicomponent solution onto Nyex™ adsorbent.

2.4.3 Adsorption Technology Design Considerations

2.4.3.1 Estimation of adsorption capacity

The adsorbed phase concentration (q) is a very important parameter which must be determined earlier on in the design. At the initial stage of the adsorption process, the adsorbent is initially free from adsorbate. At this initial stage, the system is described by a basic mass balance where the amount of adsorbate adsorbed onto the adsorbent equal the amount of adsorbate removed from the bulk solution, and is expressed as (Cooney 1999):

$$q(t) = KC(t) \qquad [2\text{-}1]$$

Where $q(t)$ (mg/g) is the concentration of adsorbate in the adsorbed phase at time, t, $C(t)$ (mg/l) is the adsorbate concentration in the liquid phase at time, t and K (m^3/kg) is the equilibrium constant.

Assuming that water molecules is not adsorbed and since the volume of contaminants is small in comparison to the volume of water, the volume of solution in the liquid phase (V) should remain constant. Hence, Eq. 2-1 can be expressed as:

$$V(C_0 - C(t)) = mq \qquad [2\text{-}2]$$

Where m is the mass of adsorbent and C_0 and $C(t)$ are the bulk liquid phase concentration at time t=0 and t=t respectively. The equation can be rearranged to give a linear relationship between the adsorbed concentration and bulk liquid phase concentration, thus resulting in:

$$q(t) = \left(\frac{C_0 - C(t)}{m}\right)V \qquad [2\text{-}3]$$

If the adsorbent was reused without completely removing the adsorbed impurities (regenerated to adsorbed phase concentration of q) the left hand side of the Eq. 9-3 would have to be replaced by $q(t)=KC(t)$, hence Eq. 2-3 reduces to:

$$m = \frac{V}{K}\left(\frac{C_0 - C(t)}{C(t)}\right) \qquad [2\text{-}4]$$

Eq. 2-4 shows that the mass of adsorbent required for adsorption can be reduced if an adsorbent with higher adsorption equilibrium constant is used. If the adsorbent at the start of the adsorption process was not initially free from impurities then the linear relationship becomes:

$$q(t) = \left(\frac{C_0 - C(t)}{m} \right) V + q_0 \qquad [2\text{-}5]$$

2.4.3.2 Batch adsorption model

Adsorption kinetics

Because adsorption is a time dependant process, it is important to understand the kinetics of an adsorption system to enable effective process design. Adsorption kinetics of liquid/solid systems are often influenced by adsorption reactions and mass transfer steps that govern the transfer of adsorbate from the bulk liquid phase to the adsorption site on the adsorbent. An adsorption kinetics study is required earlier on in the design. This study is important in analysing the rate at which the system equilibrates, as well as the adsorption mechanism.

The adsorption kinetics study is useful in describing the contaminant uptake rate which controls the residence time of contaminant uptake at the liquid/solid interface. Information on the kinetics of adsorbate uptake is also essential in selecting the optimal operating conditions for full-scale process. In order to establish the adsorption dynamics and thus the rate controlling step of the system, two widely used kinetic models namely; pseudo-first order and pseudo-second order can be used to describe experimental data (Qiu *et al.* 2009).

The resulting order of reaction should dictate the rate limiting step. A pseudo-first order fit suggests the adsorption is a diffusion based process (Onyango et al. 2004) whilst a pseudo-second order fit suggests the adsorption process is controlled by chemical adsorption (Hamdi et al. 2010).

In 1898, Lagergren presented a pseudo-first-order rate equation to describe the kinetics of liquid/solid phase adsorption of malonic and oxalic acid onto charcoal (Lagergren 1898). This representation is believed to be the earliest model relating to the adsorption rate based on the adsorption capacity. The pseudo-first-order rate equation is given as:

$$\frac{dq}{dt} = k_1 (q_e - q(t)) \qquad [2\text{-}6]$$

Where q_e and $q(t)$ are the adsorption capacity in mg/g of adsorbent at equilibrium at time t respectively and k_1 (1/min) is the first-order adsorption rate constant.

Integrating Eq. 2-6 at boundary conditions of t=0 and t=t yields:

$$\log(q_e - q(t)) = \log q_e - \frac{k_1 t}{2.303} \quad [2\text{-}7]$$

The pseudo-first-order rate constant, k_1, can be obtained from the slope of a straight line plot of $\log (q_e - q(t))$ vs. time t. The Lagergren pseudo-first order model has since been used to successfully investigate numerous adsorption systems (Ho and Mckay 1999). On several occasions, results presented in literature show that Lagergren equation is only applicable over the initial 20 to 30 minutes of the adsorption process (Ho and Mckay 1999). These issues were also highlighted by Gerente et al. (2007), who pointed out that the main disadvantage of the pseudo-first order model is that the plots are only linear over the first 30 minutes, beyond which the experimental data and theoretical results do not correlate very well. This often resulted in a theoretical q_e value that does not correlate with the experimental q_e value.

The pseudo-second order kinetic model was described in a process for the adsorption of divalent metal ions on peat (Ho et al. 2000). The main assumption for this model is that the adsorption may be second order and the rate limiting step is governed by chemisorption (adsorption step).

The pseudo-second-order rate equation is expressed as:

$$\frac{dq}{dt} = k_2 (q_e - q(t))^2 \quad [2\text{-}8]$$

Where k_2 is the second-order adsorption rate constant (g mg^{-1} min^{-1}). Integrating Eq. 2-8 at boundary conditions of t=0 and t=t yields the linearised equation:

$$\frac{t}{q(t)} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad [2\text{-}9]$$

The initial adsorption rate constant, S (mg/g min), at t = 0 can be defined as:

$$S = k^2 q_e^2$$

If the rate of adsorption is a second order mechanism, then the pseudo-second order chemisorption kinetic rate applies and a plot of $t/q(t)$ vs. t should be linear with a slope of $1/q_e$. Pseudo-second order model does not have the disadvantage of pseudo-first order model, thus eliminating the issue of using trial and error to obtain a good fit for the data (Ho and McKay, 1998).

Adsorption Isotherm

The adsorption isotherm describes the adsorption equilibrium at constant temperature and pH. It is characterised by constant values which describes the surface characteristics of the adsorbent, the mechanism of adsorption, the adsorption capacity and the affinity of the adsorbent. It is also very useful in describing the dependency of adsorbent capacity on the concentration of the contaminant. The adsorption isotherm curve defines the amount of contaminant adsorbed on the adsorbent as a function of the concentration of contaminant at equilibrium. Two very well-known and well established adsorption isotherm models known as the Freundlich and Langmuir isotherm can be used to describe the adsorption process.

The Langmuir isotherm assumes homogeneous adsorbent surface in terms of size and shape. The model also assumes homogeneous energy distribution on all active adsorption sites and the number of active adsorption sites is fixed. Another assumption is that each active site on the adsorbent can hold a maximum of one molecule and there is no interaction between molecules adsorbed on neighbouring site. The Langmuir isotherm model is defined as (Masschelein 1992; Foo and Hameed 2010):

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad [2\text{-}10]$$

In which q_e is the amount of contaminant adsorbed at equilibrium in mg/g of adsorbent with an equilibrium concentration C_e (mg/l), q_m is the maximum monolayer contaminant concentration in the solid phase in mg/g, b (l/mg) is Langmuir adsorption equilibrium constant and the Langmuir equilibrium constant, K_L (l/g), is defines as $q_m b$. The Langmuir isotherm model consists of two constants, q_m and b which can be determined by expressing Eq. 2-10 in its linear form (Eq. 2-11) and then plotting $1/q_e$ against $1/C_e$.

$$\frac{1}{q_e} = \frac{1}{q_m b C_e} + \frac{1}{q_m} \qquad [2\text{-}11]$$

One of the limitations of the Langmuir isotherm is that it assumes monolayer adsorption. However, monolayer formation is only possible at low concentration. At higher concentration, the assumption becomes negligible as contaminant molecules may attract more and more molecules towards each other.

The Freundlich isotherm model aligns with the Langmuir isotherm model over a low range of contaminant concentration in that adsorption rate is proportional to the contaminant concentration. However, at very low concentration and at very high concentrations, this linear relationship is not applicable with the Freundlich model. The Freundlich isotherm model assumes that the active site on the adsorbent, has different adsorption intensity for a particular contaminant and is not restricted to the formation of mono-layer (Abdullah et al., 2009). The Freundlich model is expressed as (Masschelein, 1992; Foo and Hameed, 2010):

$$q_e = K_f C_e^{1/n} \qquad [2\text{-}12]$$

Where q_e is the amount of contaminant adsorbed in mg/g of adsorbent with a corresponding contaminant concentration in the wastewater at equilibrium, K_f is a constant related to the adsorption capacity (l/mg) and *1/n* is the Freundlich intensity parameter. The constants in the model can be determined by reducing Eq. 2-12 to its linear form (Eq. 2-13) and plotting log q_e versus log C_e.

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad [2\text{-}13]$$

The shape of the adsorption isotherm curve provides some information about the adsorption process as well as the extent of the surface coverage by the adsorbate. The shape of the adsorption isotherm curve has been classified by Giles et al. (1960) into four basic groups and sub-groups (Figure 2.9). The adsorption isotherm curves are classified as follows:

- S curves indicate vertical orientation of the adsorbate on the surface of the adsorbent.
- L curves are associated with adsorbate molecules adsorbed flat on the adsorbent surface or molecules adsorbed vertically with strong molecular interaction.
- H curves are high affinity isotherm curves often associated with solutes adsorbed as ionic micelles and by high affinity ions exchanging with low affinity ions.
- C curves are linear isotherm curves given by solutes which penetrate into the adsorbent more readily than the solvent.

The sub-groups describe adsorbate orientation after the initial monolayer adsorption and further away from the adsorbent surface. So if the new surface generated by the adsorbed molecules has a low attraction for un-adsorbed molecules, the curve plateaus. On the other hand, if the

adsorbed layer has a strong attraction to the un-adsorbed molecules the curve does not plateau but instead rise steadily, indicating multilayer adsorption.

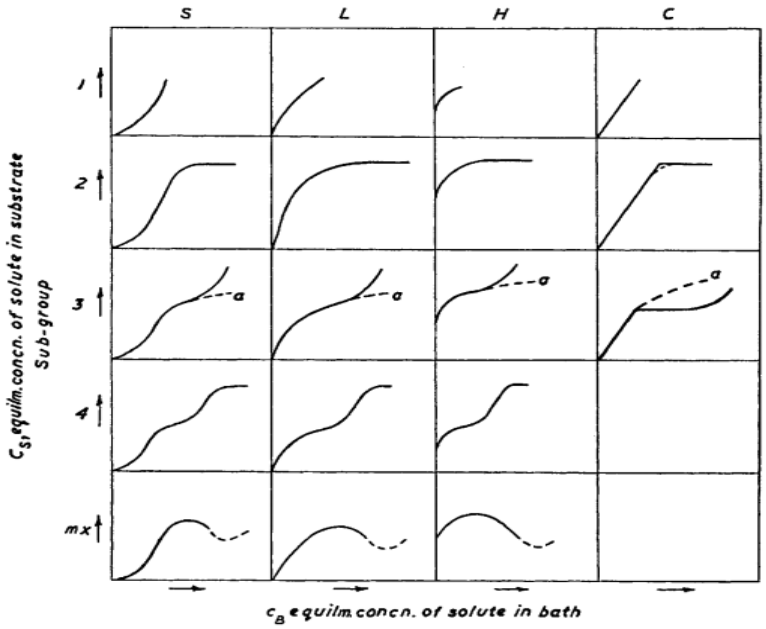


Figure 2.9 - System of adsorption isotherm classification (Giles et al. 1960)

2.4.3.3 Mass balance model

A mass balance model can be developed throughout the adsorption stages, from the transfer of adsorbent molecules from the bulk liquid phase through to the solid phase as well as within the pores of the adsorbent (intra-particle diffusion). No intra-particle adsorption is expected to occur in this process as Nyex™ is non-porous. Hence the main adsorption stages consider below are transfer of adsorbent from the bulk liquid phase and transfer through the solid/liquid interface (film diffusion). These models are discussed in detail in various literature such as Worch 2012; Fournel et al. 2010; Tien 1994; Costa and Rodrigues 1985.

2.4.3.4 Breakthrough curve model

Adsorption process can take place in either a batch or a continuous adsorption mode. Batch adsorption occurs in a closed system where a desired volume of adsorbent is added to a vessel containing a certain volume of adsorbate solution and is often used for powdered activated carbon system. The continuous adsorption occurs in an open system where adsorbate solution continuously passes through a packed or fluidised bed of adsorbent (Cooney 1999). For the

continuous adsorption process, the breakthrough curve provides the predominant information for designing the adsorption system.

When the adsorbate solution is introduced into the packed bed adsorption system, adsorbate molecules in the adsorbate solution are gradually adsorbed as they travel up the packed bed.

The adsorbent closer to the bottom of the packed bed becomes in contact with the adsorbate solution at its highest concentration level, the small amount of adsorbate molecules which escapes are then removed by the next layer of adsorbent. As the feed adsorbate solution continues to flow into the packed bed, the first layer of adsorbent becomes saturated and becomes less effective for further adsorption. Hence, the primary adsorption zone (known as the Mass Transfer Zone, MTZ) moves up through the column to regions with less saturated adsorbent (Figure 2.9). As the MTZ moves further up through the column, more and more contaminants will tend to escape into the treated adsorbate solution, the time within which adsorbate molecules escapes from the packed bed is known as the breakthrough time and the progression of the MTZ is described by the breakthrough curve (Tchobanoglous et al 2003; Cooney 1999).

The breakthrough curve is a plot of the contaminant concentration at a specific point on the system versus time, and exhibits a characteristic S shape in water and wastewater operation, but with varying degree of steepness (Figure 2.10). The shape of the breakthrough curve is important in determining the optimum operating parameters of the system. Factors affecting the shape of the curve are all the same as those affecting the adsorption. The breakthrough time is decreased by:

1. Increased particle size of the adsorbent
2. Increased concentration of the adsorbate solution
3. Increased flow-rate, and
4. Decreased packed bed depth

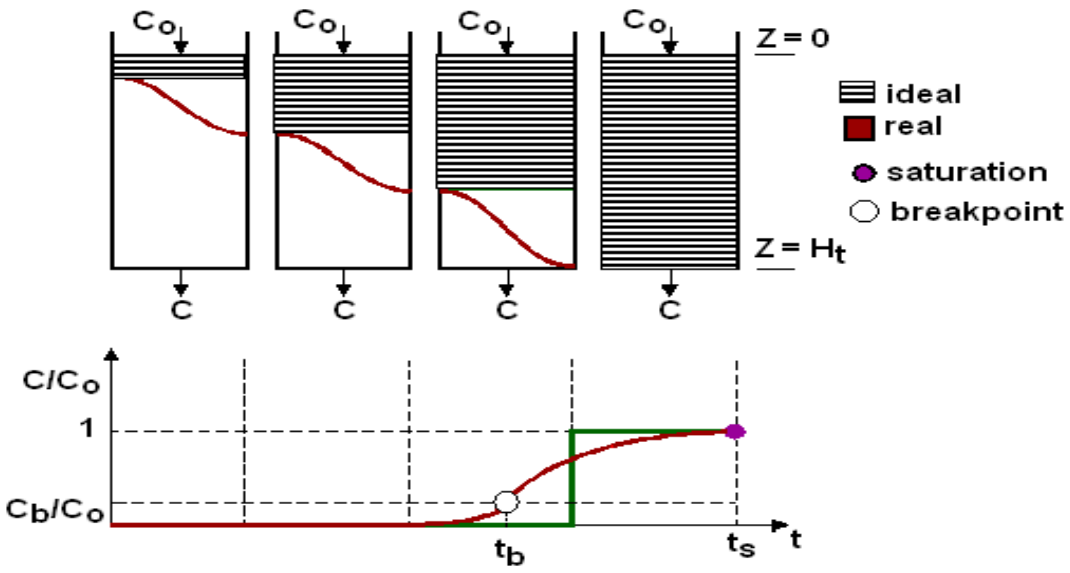


Figure 2.10 - Breakthrough Characteristics of a Fixed-Bed Activated Carbon Adsorber (Barros et al. 2013)

The breakthrough curve can either be determined experimentally or through mathematical modelling. Various different mathematical models are available to predict the breakthrough behaviour of a packed bed adsorber system. These models can be classified as either a kinetic model or a scale up model.

Kinetic Model of Packed Bed

Three well known kinetics models, Thomas, Yoon-Nelson and Adam-Bohart are often used to predict the breakthrough curve as well as to determine the characteristic parameters of the packed bed useful for process design.

The Thomas model is one of the most widely applied to estimate the adsorptive capacity of adsorbent. The derivation of the model assumes second-order reversible reaction kinetics and the Langmuir isotherm. The expression for Thomas model is given by (Thomas 1944):

$$\frac{C(t)}{C_0} = \frac{1}{1 + \exp\left[\frac{K_{Th}}{Q_f}(qm - C_0 V)\right]} \qquad [2\text{-}14]$$

Where K_{Th} (l/min.mg) is the Thomas model constant, C_0 and $C(t)$ are the initial and effluent solution concentration (mg/l) respectively, q (mg/g) is the adsorption capacity, m is mass of adsorbent (g) and Q_f is influent flow rate (l/min). The constants in the model can be determined

by reducing Eq. 2.14 to its linear form (Eq. 2.15) and plotting *ln (C_0/C(t)-1)* versus *t*. The linear form of Thomas model is expressed as:

$$\ln\left(\frac{C_0}{C(t)}-1\right)=\left(\frac{K_{Th}qm}{V}-K_{Th}C_0t\right) \qquad [2\text{-}15]$$

Yoon-Nelson model is a fairly simple model and requires no data on the characteristics of the adsorbate and adsorbent, as well as the parameters of the packed bed. However, the model is not very useful in obtaining process variables and predicting adsorption for a variety of process variables. The Yoon-Nelson model assumes that decrease in the probability of each contaminant to be adsorbed is proportional to the probability of its adsorption and breakthrough on the adsorbent and is represented by (Yoon and James, 1984):

$$-\frac{dC}{dt}=K_{YN}(t-\tau) \qquad [2\text{-}16]$$

Where K_{YN} (1/min) is the rate constant and τ (min) is the time required for 50% adsorbate breakthrough. Constants K_{YN} and *t* can be determined by expressing Eq. 2-16 in its linear form (Eq. 2-17) and then plotting *ln ($C(t)/C_0 - C(t)$)* against time (*t*).

$$\ln\left(\frac{C(t)}{C_0-C(t)}\right)=K_{YN}(t-\tau) \qquad [2\text{-}17]$$

The Adam-Bohart model (Bohart and Adams 1920) hypothesised that the rate of adsorption is proportional to both the concentration of the adsorbate in the bulk liquid phase and the residual capacity of the adsorbent. The model can be expressed as:

$$\frac{C(t)}{C_0}=\exp\left(K_{AB}C_0t-K_{AB}q_{\max}\frac{z_b}{u}\right) \qquad [2\text{-}18]$$

Where K_{AB} (l/min.mg) is rate constant of Adams-Bohart model, q_{max} (g/l) is maximum adsorption capacity per unit volume of adsorbent, *u* (m/min) is the velocity of influent solution and z_b (m) is the bed depth. The linear form of the equation can be expressed as:

$$\ln \frac{C(t)}{C_0} = \left(K_{AB} C_0 t - K_{AB} q_0 \frac{z_b}{u} \right) \quad [2\text{-}19]$$

The constants of the Adam-Bohart equation can be obtained from the slope and intercept of a straight line plot of *ln (C(t)/C₀)* against time *t*.

Scale-up model (Length of unused bed)

Once the adsorption process is stopped at the breakthrough point, a proportion of the adsorbent bed remains unused. The length of unused bed (LUB) model uses the length of unused bed at the breakthrough point to characterise the breakthrough behaviour. The LUB is proportional to the distance between the packed bed height (z_b) and the location of the stoichiometric front (h_{st}) and is given by (Thomas and Crittenden 1998; Faust and Aly 1987):

$$LUB = z_b - h_{st} \quad [2\text{-}20]$$

The stoichiometric front is a representative of when the actual capacity of the adsorbent bed is used up and it's the point that breaks the MTZ into two equal section.

The LUB model is related to the adsorption rate in that the slower the mass transfer rate between the adsorbate and adsorbent, the longer the LUB. Since the stoichiometric and the actual front travels at the same velocity, the traveling velocity of the MTZ (v_z) can be expressed using the real or stoichiometric time (Thomas and Crittenden 1998), thus:

$$v_z = \frac{h_{st}}{t_b} = \frac{z_b}{t_{st}} \quad [2\text{-}21]$$

Where t_b is the breakthrough time and t_{st} can be determined by integrating the breakthrough curve as follows (Faust and Aly 1987):

$$t_{st} = \int_0^t \left(1 - \frac{C_0}{C_t} \right) dt \quad [2\text{-}22]$$

Combining the above equation with the LUB (Eq. 2-20) gives:

$$LUB = v_z\left(t_{st} - t_b\right) = z_b \frac{t_{st} - t_b}{t_{st}} \qquad [2\text{-}23]$$

The LUB model can be used to estimate the length of unused bed on the basis of an experimentally determined breakthrough curve. The estimated LUB can be used to determine the actual bed length required in full scale system. In order to scale up an adsorption process, the desired breakthrough time must first be defined.

2.5 Electrochemical Regeneration Process

2.5.1 Introduction to electrochemical reaction

An electrochemical reaction is a chemical reaction brought about as a result of the transfer of electrons between electrodes and species in solution (Grimshaw 2000). Initially, unpaired electrons attach to molecules in the substrate to form reactive intermediates, these reactive intermediates are then transformed into electrically charged ions. The transformation of reactive intermediates involve a sequence of bond forming and bond cleaving reactions, and the process by which chemical species are transformed to electrically charged ions is termed electrolytic dissociation (Bard and Faulkner 2000; Oldham and Myland 1994; Grimshaw 2000). The reaction which occurs during the electrolytic dissociation process is called an electrochemical reaction.

An electrochemical reaction system requires both a cathode and an anode electrode. The ions formed in the process move in an electric field as a result of their charge. The type of electrochemical cell used for the electrolytic dissociation process is known as an electrolytic cell, which means electrochemical reaction only occurs when energy is applied. Once energy is applied across the cell, electrons enter the electrochemical system via the negatively charged cathode, and leaves through the anode.

In addition to the electrodes, the system also requires an electrolyte to conduct electricity by providing ions that flows to and from the electrode when energy is applied (Perez 2004; Garnett and Treagust 1992). During electrochemical reaction, species at the anode undergo oxidation reaction and those at the cathode reduction reaction. The application of various electrochemical techniques in water and wastewater treatment are reviewed in the following section as well as the mechanism of electrochemical reaction focusing particularly on electrochemical oxidation reaction, which is used in the Arvia™ process.

2.5.2 Electrochemical technologies in water and wastewater treatment

Industries are facing increasing pressure to meet more stringent effluent legislations, this has resulted in elevated demands for economical and environmentally friendly treatment processes. Electrochemistry offers a promising alternative for wastewater treatment and is finding increasing use in treatment purposes such as metal ion removal and recovery, as well as

removing organic contaminants from industrial wastewaters (Bazan and Bisang 2004; Panizza et al. 2000; Israilides et al. 1997; Naumczyk et al. 1996; Savall 1995; Campbell et al 1994). Electrochemical treatment processes can be cost effective, energy efficient and is environmentally friendly as it produces no waste and does not require use of harmful chemicals. Another advantage of the electrochemical process is that controlling the applied voltage enables selective treatment in which a specific pollutant is targeted, thus the production of by-products from electrochemically active species can be avoided (Jüttner et al. 2000; Rajeshwar et al. 1994). However, there are some disadvantages of electrochemical process where in some cases a high operating voltage is required which result in high operating cost, there is also the potential for the formation of toxic products and risk of electrode corrosion resulting in operational issues and potential contamination (Anglada et al. 2009). Various electrochemical techniques have so far been applied for removal of various contaminants from water and wastewater, this includes:

Electrodialysis

Electrodialysis is a versatile process used for removing ions and ionisable species from aqueous solution and is often applied to deionisation/desalinisation of aqueous solution as an alternative to reverse osmosis. It is an electro-membrane process which uses ion permeable anion membrane and cation membranes, which under the influence of an electric field has the ability to selectively transport negative (anion) and positive (cation) charged ions respectively in order to achieve separation of electrolytes. Two types of chambers are created, the concentrate chamber which holds high ionic concentration and the diluate chamber holding the low ionic concentration solution. The main application of electrodialysis is in the production of potable water from brackish water or seawater (Lee et al. 2002). Other applications include the regeneration of ion exchange resin (Dermentzis and Ouzounis 2008; Meng et al. 2004) and treatment of radioactive wastewater in nuclear plants (Inoue et al. 2004). Although electrodialysis is effective at removing low molecular weight ionic components, non-charged higher molecular weight compounds will not be significantly removed. The process also becomes less economical when the influent/feed solution has low conductivity as there are fewer ions available in solution to carry current which means ion transport and energy efficiency decreases (Sistat et al. 2008; Tanaka 2004; Suendo et al. 2001; Strathmann et al. 1997; Taky et al. 1992).

Electrodeionisation

Electrodeionisation process eliminates the disadvantages of the electrodialysis process by using ion exchange resins to concentrate the ions as well as to act as an ion bridge thus increasing the overall conductivity of the system (Ervan and Wenten 2002). The treatment process of electrodeionisation consist of two steps. In the first step of the process, ions are bound by the ion exchange resin and in the second step, ions bound to the ion exchange resin are transported through the ion exchange membrane into the concentrate chamber (Ganzi et al. 1992). As a result of the increased conducting nature of the electrodeionisation process, it can be used in the production of ultra-pure water used in food or pharmaceutical processing (Lee et al. 2003; Wang et al. 2000).

Electrocoagulation

Electrocoagulation is an electrolytic process used for treating organic and inorganic wastewater with the tendency to coagulate. It has been applied in removing contaminants that are difficult to remove by filtration and chemical treatment systems such as wastewater containing oil and grease, dyes, suspended solids and heavy metals (Kuokkanen et al. 2013; Merzouk et al. 2009; Canizares et al. 2006; Chen 2004; Biswas and Lazarescu 1991). Electrochemical coagulation offers an alternative to coagulation process in that it does not require chemical coagulation agent as this is generated in situ by electrolytic oxidation of the appropriate species. The process utilises sacrificial metal electrodes such as iron and aluminium (Mollah et al. 2004) to produce metal ions which then diffuse into the bulk solution to be treated. These metal ions are further hydrolyse to form coagulants which interact with charged ionic contaminants in the bulk solution to facilitate coagulation and resulting in precipitation of contaminants from the aqueous phase.

Electrofloatation

Electrofloatation is the process of removing pollutants from water through the electrolytic formation of fine bubbles which collects contaminants from the bulk solution and carry them to the surface of the solution where they are removed by skimming. Electrofloatation is often combined with electrocoagulation technique, where coagulated species are brought to surface using electrofloatation technique (Wang et al. 2009; Zuo et al 2008; Gao et al. 2005; Ge et al. 2004; Chen et al. 2000). The process has been applied for the removal of oils and other low density emulsions and suspended solids from wastewater (Merzouk et al. 2009; Bande et al.

2008; Khelifa et al. 2005; Hosny 1996; Mraz and Krýsa 1994; Hosny 1992; Ho and Chan 1986).

Electrolytic wet air oxidation

Wet oxidation is the oxidation of dissolved or suspended contaminants in aqueous solution using oxygen as the oxidiser. Electrolytic wet oxidation is a novel process which integrates wet oxidation and electrolytic reaction. The oxidation reaction is often catalysed using very high temperature and pressure which means high operating cost (Serikawa et al. 2000).

Electrochemical oxidation

Electrochemical oxidation is a widely studied technique used in the removal of organic contaminants in wastewater. It involves the oxidation of organic contaminants in the anode of an electrolytic cell by the action of in-situ electrochemically generated oxidants. Extensive investigation of this technology started around the late 1970s (Martinez-Huitle 2004) and interest have since continued to grow especially for wastewater possessing high electric conductivity, whilst addition of electrolyte is required for the treatment of low conducting wastewater (Manisankar et al. 2003, Bejankiwar, 2002). Over the last two decades, research work has been focused on the efficiency of oxidising different organic pollutants on different electrodes (Kuhn 1971). Some of the more recent research report findings on the electrochemical oxidation of phenol (Canizares et al. 2005; Gherardini et al. 2001; Iniesta et al. 2001) polyvinyl alcohol (Kim et al. 2003), naphthalene sulphonates (Panizza et al. 2006), oxalic acid (Scialdone et al. 2009), benzoic acid (Velegraki et al. 2010), acid orange 7 (Hammami et al. 2008) and salicylic acid (Guinea et al. 2008).

Study on electrochemical reaction process has highlighted a number of disadvantages in its application (Anglada et al. 2009; Murphy et al. 1992; Canizares et al. 2003):

- Difficulty in treating wastewater with very low organic concentration
- Treatment of wastewater with high organic concentration can be energy intensive
- Low electric conductivity of wastewater solution result in high operating voltage

When the organic concentration of the wastewater is very low, mass transfer of reactant to the surface of the electrode is limited thus making it difficult to treat electrochemically. As mentioned earlier, the conductivity of the wastewater can be increased by adding an electrolyte such as NaCl. However, NaCl cannot be removed by the electrochemical reaction process thus

increasing the dissolved solid content of the treated wastewater which limits its reuse. The use of adsorption technique to concentrate the contaminants in wastewater using a highly conducting adsorbent material, known as Nyex™, has been proposed by Brown (2005). The Nyex™ adsorbent eliminated the disadvantages mention earlier by acting as both a conducting bridge to reduce or eliminate the need for NaCl in low conduction wastewater solution and a concentrating medium to increase the contaminant concentration in solution. This therefore results in a reduction in the cell potential, and thus operating cost.

2.5.3 Classification of electrochemical oxidation reaction

The electrochemical regeneration process involves the electrochemical oxidation of adsorbed organic contaminants, which is believed to be a result of both direct and indirect oxidation. Direct electrochemical oxidation of organics occurs on the surface of the anode either through direct electron transfer or through the action of hydroxyl radicals. Whilst indirect electrochemical oxidation describes oxidation of organics in the bulk liquid phase, by species that have been oxidised at the anode (Jüttner et al. 2000). The mechanisms for both direct and indirect oxidation are further discussed in the following section.

Direct oxidation

The most accepted hypothesis for direct electrochemical oxidation is that two oxidation pathways are involved. It has been proposed by Comninellis (1994) that the two pathways are both associated with the generation of hydroxyl radicals at the surface of the anode either from the deposition of acidic species (Eq. 2-24) or from direct conversion of hydroxyl ions in alkaline solution (Eq. 2-25) (Canizares et al. 1999).

$$2H_2O \rightarrow 2OH^{\bullet} + H^{+} + e^{-} \qquad [2\text{-}24]$$

$$OH^{-} \rightarrow OH^{\bullet} + e^{-} \qquad [2\text{-}25]$$

The radicals generated can either be physically or chemically adsorbed on the anode depending on the nature of the used anode electrode material (Martinez-Huitle 2006). Two types of anode has been identified, namely active and non-active (Iniesta et al. 2001). In both cases, the first reaction is the oxidation of water molecules on the electrode leading to the formation of hydroxyl radicals (Eq. 2-26).

$$M + H_2O \rightarrow M(OH^{\bullet}) + H^+ + e^- \quad [2\text{-}26]$$

At active electrode, there is a strong interaction between the active sites on the electrode (M) and the hydroxyl radicals (chemical adsorption). This may result in the adsorbed hydroxyl radical interacting with the electrode to form a higher oxide, MO (Eq. 2-27).

$$M(OH^{\bullet}) \rightarrow MO + H^+ + e^- \quad [2\text{-}27]$$

The chemically adsorbed hydroxyl radicals can participate in the selective oxidation of organics (R) to form products with slow oxidation kinetics (Eq. 2-28). This oxidation pathway is known as electrochemical modification as organics are modified but not completely removed from solution. The electrochemical modification reaction is in direct competition with a side reaction generating oxygen through the decomposition of higher oxide (Eq. 2-29).

$$MO + R \rightarrow M + RO \quad [2\text{-}28]$$

$$2MO \rightarrow 2M + O_2 \quad [2\text{-}29]$$

With non-active electrode, weak physical interaction is formed between the hydroxyl radicals and the electrode. Hydroxyl radicals generated on the surface of non-active electrodes have a very high oxidation potential and can achieve complete oxidation of organics to carbon dioxide and water, hence this oxidation pathway is known as electrochemical cold combustion (Eq. 2-30). Again, like the electrochemical modification method, the electrochemical cold combustion reaction also faces direct completion with a side reaction producing oxygen without any participation of the electrode (Eq. 2-31).

$$M(OH^{\bullet}) + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \quad [2\text{-}30]$$

$$2M(OH^{\bullet}) \rightarrow 2M + O_2 + H^+ + e^- \quad [2\text{-}31]$$

The highly oxidising hydroxyl radical can also combine to form hydrogen peroxide (Eq. 2-32) which can then be further oxidised to oxygen (Eq. 2-33) (Marselli et al. 2003).

$$2OH^{\bullet} \rightarrow H_2O_2 \qquad [2\text{-}32]$$

$$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^- \qquad [2\text{-}33]$$

Other reaction route which has been proposed include formation of organic radicals which is then oxidised as shown in Eq. 2-34 to 10-36 (Comninellis 1994).

$$RH + OH^{\bullet} \rightarrow R^{\bullet} + H_2O \qquad [2\text{-}34]$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad [2\text{-}35]$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad [2\text{-}36]$$

A schematic illustration of these routes is shown in Figure 2.11.

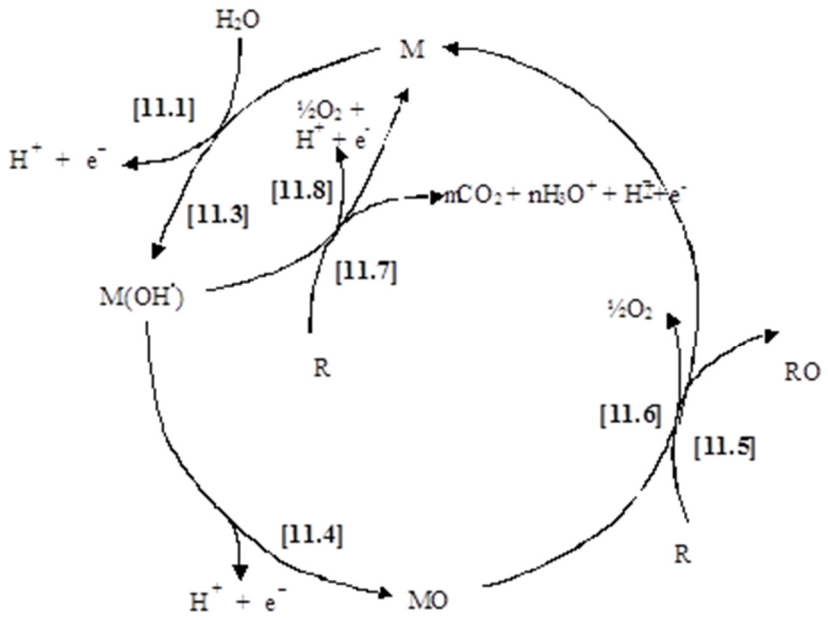


Figure 2.11- Hydroxyl radical formation and destruction for direct electrochemical oxidation mechanism; during conversion and combustion of organic compounds at active and not active anodes (Comninellis 1994)

Indirect oxidation

In the process of indirect oxidation, an electrochemically oxidised species generated at the anode act as a mediator for the oxidation of organics. The most frequently used electrochemical oxidant are chlorine or hypochlorite (Pyo and Moon 2005). Other electrochemical oxidant which can also be used includes ozone, peroxide, Fenton's reagent and peroxodisulphate (Jüttner et al. 2000).

The presence of NaCl in wastewater solution is known to increase the rate of electrochemical oxidation of organic contaminants through indirect oxidation. Sodium chloride can either be present in saline wastewater or added as an electrolyte to reduce operating voltage. In a study by Lin et al. (1998), it was found that at low salt concentration, direct electrochemical oxidation is the dominant process, while at high salt concentration indirect electrochemical oxidation becomes more significant. The study also showed that increasing the salt concentration from 0.5% to 3.5% increase the percentage removal of COD from 31.2% to 74% respectively.

A possible mechanism of the indirect electrochemical oxidation can be described through the formation of adsorbed chlorohydroxyl radicals on the electrode and can be described by Eq. 2-37.

$$M + H_2O + Cl^- \rightarrow M(ClOH) + H^+ + 2e^- \qquad [2\text{-}37]$$

These chlorohydroxyl radicals can then react with organic contaminants and chloride ions according to Eq. 2-38 and 2-39.

$$M(ClOH) + R \rightarrow M + RO + Cl^- + H^+ + 2e^- \qquad [2\text{-}38]$$

$$M(ClOH) + H_2O + Cl^- \rightarrow M + O_2 + Cl_2 + 3H^+ + 4e^- \qquad [2\text{-}39]$$

Above a pH of 7, the free chlorine produced can react with hydroxide ions present in the system to form hypochlorite (equation 2-40).

$$Cl_2 + 2OH^- \rightarrow H_2O + OCl^- + Cl^- \qquad [2\text{-}40]$$

Chlorine, oxygen and hypochlorite are the primary oxidants formed through direct electrochemical oxidation. Free chlorine and oxygen can further react at the anode to produce secondary oxidants such as ozone, hydrogen peroxide and chlorine dioxide. The

chlorohydroxyl radicals formed in the initial process have a very short like due their high oxidation potential (weak oxidant). Hence they are either able to directly oxidise organics on the surface of the anode or are decomposed to form primary or secondary oxidants which then diffuse away from the anode to take part in indirect oxidation (Chatzisymeon et al. 2006).

The rate of indirect oxidation is therefore proportional to the diffusion rate of oxidants from the anode to the bulk liquid phase. These routes are illustrated schematically in Figure 2.12.

Direct electrochemical oxidation using non-active electrode is often proposed as the most effective oxidation process for removing organic contaminants from low saline wastewater solution as the oxidants produced in indirect oxidation may not be able to achieve complete combustion.

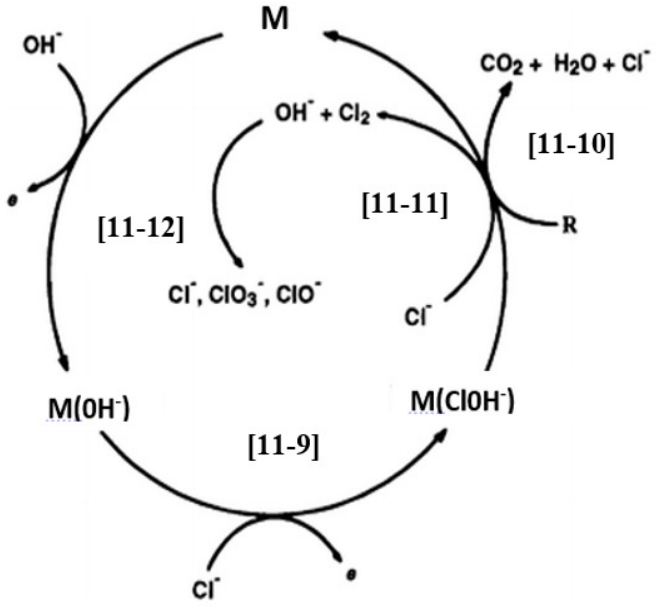


Figure 2.12 - Schematic depicting the reaction mechanism proposed for the indirect electrochemical oxidation of organics (Martinez-Huitle and Ferro 2006)

2.5.4 Electrochemical regeneration of GICs

Published literature on the electrochemical regeneration of GICs are limited to those undertaken for Nyex™ adsorbent, no other form of GICs have to date been investigated (Asghar et al. 2013; Hussain et al. 2013; Asghar et al. 2012b; Conti-Ramsden et al. 2012a,b; Brown and Roberts 2007; Brown et al. 2004a,b). A comprehensive study conducted by Brown

et al. (2004a) on the electrochemical regeneration of a GIC adsorbent demonstrated the following:

- Increasing the thickness of the adsorbent bed resulted in high cell potential requirement due to increased ohmic drop across the bed. Although the inter electrode distance from which high regeneration efficiencies can be achieved is greater than normal due to the electrical conductivity of the Nyex™.
- Regeneration efficiency increase with current density but a reduction in regeneration efficiency was observed as the current density is increased over 20 mA/cm^2. This reduction in regeneration efficiency was likely due to an increase in side reactions that occur at higher voltages.
- Regeneration efficiency increased with charge passed, however no further increase was noted above a charge of 25 C/g.
- Increasing the electrolyte concentration leads to increased regeneration efficiency up until around 3% sodium chloride concentration, after which no additional benefit was observed.

In general, the optimum operating parameters proposed are current density of 20 mA/cm^2, charge of 25 C/g, and a 3% sodium chloride concentration. A key finding in this research is that that a 100% regeneration of the adsorbent capacity was achieved within a very short time of around 10 minutes.

Since the GICs act as an anode in the electrochemical cell, it is highly likely that electrochemically formed oxidising agents such as chlorine and hypochlorite are attached to the surface.

Study showed that rinsing the GIC adsorbent to remove adsorbed oxidising species before re-adsorption increased the adsorption capacity (Brown et al. 2004a). SEM photographs of the GIC surface after regeneration showed that there is no formation of internal pores and the rough surface observed after regeneration provide evidence of shearing of some graphene layers thus resulting in the reduction of particle size distribution (Brown et al. 2004a).

2.5.5 Electrochemical disinfection process

Electrochemical disinfection is the removal of microorganisms using disinfection species generated during the electrochemical oxidation process described in the previous section. In

electrochemical disinfection, current is applied between the anode and cathode electrodes placed in an electrochemical cell.

The disinfection efficiency of the process depends on the configuration of the electrochemical cell, the material of the electrodes, the electrolyte composition, influent flowrate, electric current and the microorganisms being destroyed (Kerwick et al. 2005). Previous research conducted to determine the mechanism of electrochemical disinfection has proposed several mechanisms such as cell death due to electrochemically produced oxidants, irreversible permeabilization of cell membrane by the applied electric current and electrochemical oxidation of vital cellular constituents by the applied electric current (Weaver and Chizmadzhev 1996). Of all of the proposed mechanisms, destruction of microorganisms due to electrochemical production of oxidants (especially chlorine) is the most considered mechanism (Jeong et al. 2006) and is reviewed in the following section.

2.5.5.1 Disinfection by electro-chlorination

When electrochemical disinfection is applied to water containing chloride ions its effect is considered to be based mainly on the electrochemical production of hypochlorite and/or hypochlorous acid through oxidation of chloride ions present in the water (Krstajić et a. 1987; Kelsall 1984). The effectiveness of the electro-chlorination mechanism, increase for water which contains high concentration of chloride ions. However, previous research has demonstrated effective electro-chlorination using water containing low concentration of chloride ions (Kraft et al. 1999, Nakajima et al. 2004, Bergmann and Koparal 2005). The production of disinfectant (hypochlorite/hypochlorous acid) occurs in a side oxidation reaction as expressed by the following reaction mechanism (Krstajić et al. 1987):

$$2Cl^- \rightarrow Cl_2 + 2e^- \qquad [2\text{-}41]$$

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad [2\text{-}42]$$

$$HClO \Leftrightarrow ClO^- + H^+ \qquad [2\text{-}43]$$

In the reaction molecular chlorine (Cl_2) is initially produced by the electrochemical oxidation of chloride ions present in the water. The chlorine generated is then hydrolysed in water to form hypochlorous acid (HClO), the hypochlorous acid dissociates into hypochlorite anion (ClO^-) forming a pH dependent equilibrium equation (Eq. 2-43).

The plot in Figure 2.13 illustrates the availability of disinfecting chlorine species as a function of pH. The plot shows that at a pH value below 3 the solution exist as a mixture consisting predominantly of Cl_2. At a pH range of 4 to 6 HOCl becomes the predominant species, whilst at pH above 6, ClO^- starts to form and become the dominant species.

The total hypochlorite and hypochlorous acid generated is often defined as the free chlorine. The overall disinfection effect of the free chlorine is based on the formation of atomic oxygen according to the reaction (Krstajić et al. 1987):

$$HClO = O + Cl^- + H^+ \quad [2\text{-}44]$$

$$ClO^- = O + Cl^- \quad [2\text{-}45]$$

It can be noted that in the above equation, chloride ions which have been used up for electrochemical production of free chlorine is reformed. Hence there is no overall change in the composition of the water during electrochemical disinfection.

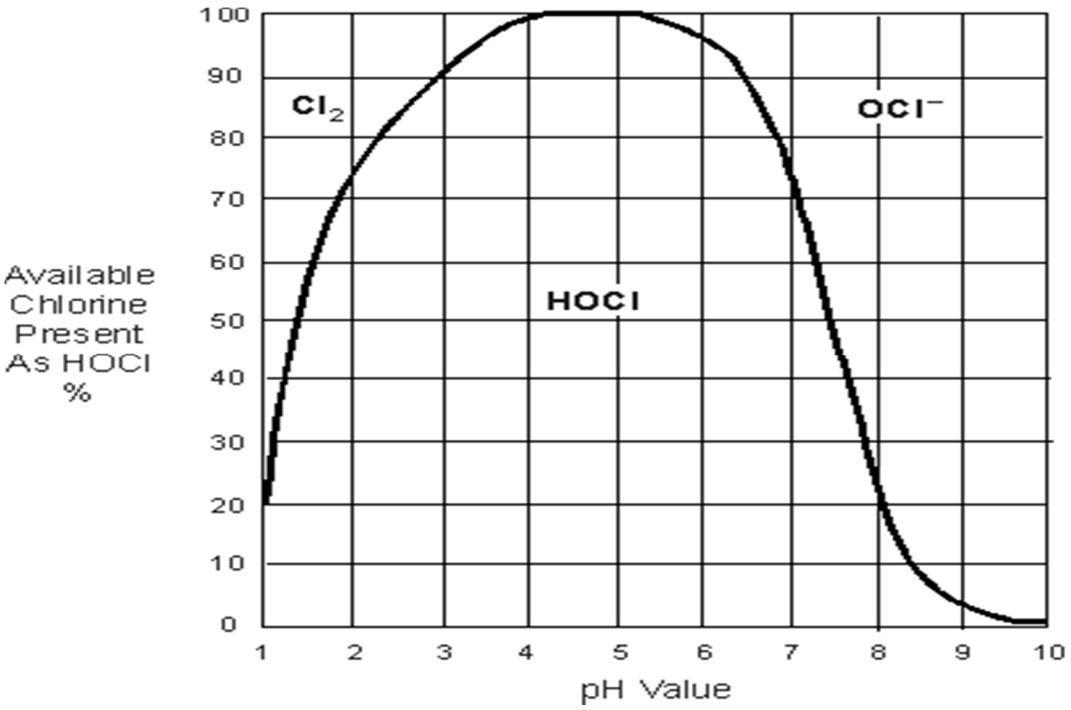


Figure 2.13 - Relationship between free available chlorine and pH (Source, Aquaox 2014)

2.5.5.2 Disinfection by ozone production

In cases where zero chloride ion concentration is required in the influent and effluent water, the production of free chlorine cannot take place. Thus, electrochemical disinfection relies on the production of other disinfecting species. In-situ production of ozone can be achieved in the system by using anode electrode with high oxygen overvoltage, high electric current and low water temperature. The direct ozone production can be described using the reaction equation (Jeong et al. 2006):

$$3H_2O = O_3 + 6e^- + 6H^+ \quad [2\text{-}46]$$

2.5.5.3 Disinfection by hydrogen peroxide

Unlike free chlorine and ozone disinfectants, the production of hydrogen peroxide takes place at the cathode. This process have been successfully utilised for water disinfection and can be expressed using the reaction equation (Jeong et al. 2006; Santana et al. 2005):

$$O_2 + 2H_2O + 2e^- = H_2O_2 + 2OH \quad [2\text{-}47]$$

Dissolved oxygen in water serves as the main source of oxygen for the reaction, although oxygen generated from direct electrolysis of water can also be used for the production of hydrogen peroxide (Rajeshwar et al. 1994; Dhar et al. 1982).

The disinfection potential of an electrochemical disinfection system is governed by the oxidant role of the reactive oxygen species produced by water discharge, these species are responsible for the inactivation of microorganisms (Martinez-Huitle and Brillas, 2008). The ozone and hydrogen disinfectant has a higher disinfection potential than free chlorine due to the high oxidation potential of their reactive oxygen species. However, the very short life of the reactive oxygen species means disinfection can only take place at the surface of the electrode and not within the bulk of the liquid, thus the overall disinfection effect or capacity is fairly small (Jeong et al. 2006; Polcaro et al. 2007).

2.6 Heat Recovery Processes

2.6.1 Introduction

In the UK energy used in homes accounts for 29% of total energy usage and carbon dioxide (CO_2) emission in 2013 (Prime et al. 2014). More energy is used in homes than in industry (Prime et al. 2014), thus indicating that energy recovery in the home presents a major opportunity to cut energy use and CO_2 emission. Around 53% of energy used in homes are used for heating purposes with the predominant contribution of heat coming from space heating (75%) and water heating (21%), accounting for 96% of total heat demand (DECC 2012) (Figure 2.14). Nearly all homes in the UK are designed to use boilers for heating, these boilers are fuelled mainly by natural gas which is the source of 80% of heat consumption (Prime et al. 2014) (Figure 2.15). Although effort has been made to enhance the efficiency of home energy usage and some progress have been made in the past decade, it is still a challenge to achieve the EU requirement of obtaining 15% of all energy from renewable source as well as a 34% cut in greenhouse emission by 2020 (Palmer et al. 2011).

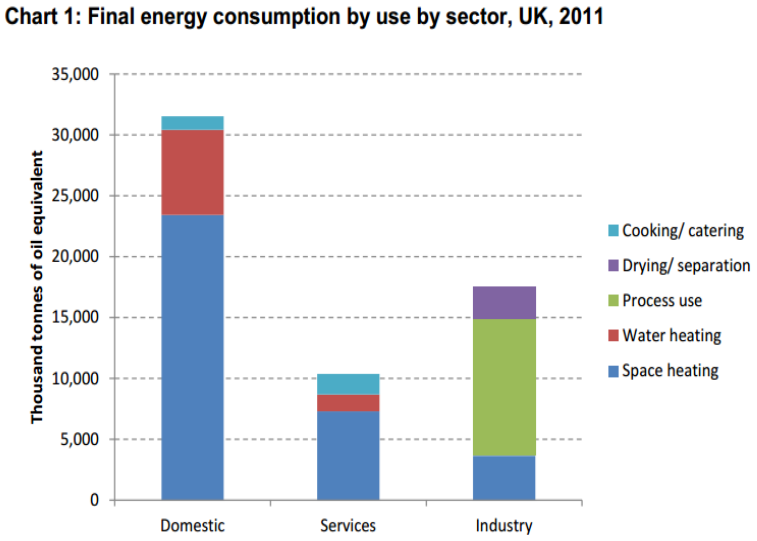


Figure 2.14 - Final energy consumption in the UK based on use by sector (DECC 2012)

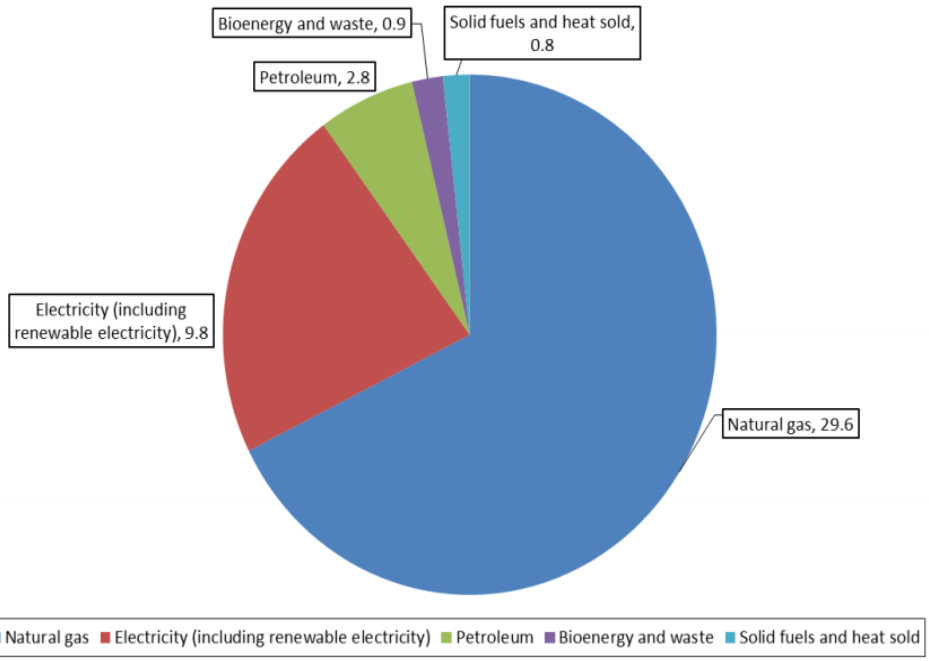


Figure 2.15 - Domestic consumption by fuel (mtoe), UK 2013 (Prime et al. 2014)

A high percentage of the energy used for water heating in homes exists in grey water, such as grey water generated in the bathroom, dishwasher and washing machine. However, this energy is often discharged into the environment without being recovered. Incorporating heat recovery to capture this energy will increase the cost saved by consumers and thus make the system more attractive to consumers.

Heat recovery is the collection and reuse of heat taken from a process that would otherwise be lost. Heat recovery system utilises heat transfer method to transfer heat from a high heat source to a low heat source. Thus in order for heat transfer to occur, a temperature difference must exist between the two systems. The fundamental modes of heat transfer are conduction, convection and radiation (McCabe et al. 1993). When a temperature gradient exists in a stationary medium which may be a solid or fluid, the heat transfer occurring across the medium is termed conduction. In contrast, the term convection is used to describe heat transfer which occurs between a surface and a moving fluid when a temperature gradient exists between the surface and moving fluid. Thermal radiation is a type of electromagnetic radiation which can be emitted or absorbed by all surfaces. Hence in the absence of an intervening medium, heat transfer by radiation may occur between two surfaces at different temperature.

In general, heat is transferred in solid by conduction, in liquid by conduction and convection and in open space by radiation. The conduction and convection mode of heat transfer is covered

extensively in numerous literatures such as Incropera 2011, Potter and Hotchkiss 1995, Coulson et al. 1996.

2.6.2 Heat recovery processes

The principle of heat transfer is widely used in many industrial processes. Various forms of heat exchanger equipment are commonly used for the transfer of heat from one medium to another. Heat transfer equations discussed in the previous section are applied in the design of a heat exchanger in order to estimate the transfer of energy for effective heat transfer under controlled conditions. The various forms of heat exchanger used in industry are briefly discussed in the following section.

2.6.2.1 Counter flow heat exchangers

Continuous flow heat exchangers form the most important class of heat exchangers (Potter and Hotchkiss 1995). In this case, both of the fluids exchanging heat are moving continuously through the system and acquiring or giving up heat. One of the fluids is passed through pipes and the other fluid passes across or round the pipe. The temperature difference between the two fluids is the main factor controlling the rate of heat transfer. Flow of the two fluids can occur through numerous ways, if both fluid flows in the same direction the system is classified as parallel flow exchanger. In the case of both fluids flowing in opposite direction, the system is classified as counter flow, and if the fluid flows in right angle or perpendicular to each other the system is classified as cross-flow (Potter and Hotchkiss 1995). Counter flows are often preferred as the temperature of the exiting stream approaches the temperature of the entering stream, thus resulting in a high heat transfer rate.

2.6.2.2 Plate heat exchangers

Plate heat exchangers are the most common heat exchanger used for fluids with low viscosity (Coulson et al. 1996). Heating and cooling fluids flow through alternative passages between plates which are clamped and separated by gaskets. Each plate have a number of troughs positioned at right angle to right angle to the direction of flow and arranged so they interlink to form channels of constantly changing flow direction. The gaskets incorporated into the system also control the flow and can allow parallel or counter current flow depending on their design (Potter and Hotchkiss 1995). The advantage of this system is that it provides a large heat

transfer surface that is easy to clean (Coulson et al. 1996). The high heat transfer coefficient of these heat exchangers enables them be operated using fluids with very small temperature difference, so that a high heat recovery can be obtained.

2.6.2.3 Heating coil heat exchangers

This is a fairly simple form of heat exchanger where a coil is immersed in a tank or wrapped around the tank. The heat transfer process occurs by either passing hot fluid through the coil which is immense in cold water, or by passing cold fluid through the coil immense in hot fluid. In either case, some form of agitation is used to obtain better distribution in the tank. The thermal resistance in this system arises from water film on the inside of the coil, the wall of the tube, the film on the outside of the coil and any scales that may be present within or on the surface of the coil (Coulson et al. 1996).

2.6.2.4 Grey water heat recovery systems

In grey water heat recovery, heat extracted from the shower/bath, washing machines and dishwasher is used to warm incoming mains water, thus reducing pressure on the boiler and energy required for water heating. Previous studies have shown significant potential for heat recovery from grey water. Heat from grey water can be recovered, either by passing the grey water through a coil immersed in mains water (combined system) or by passing mains water through a coil wrapped around a drainage pipe (drain heat recovery system). In the combined unit, heat is transferred to mains water stored in a tank by conduction and convection using a heat exchanger. On the other hand, the drainage system uses a heat exchanger unit to transfer heat directly from the drainage system. Study conducted by Eslami-nejad and Bernier (2009) demonstrated that 21.5% heat recovery can be obtained by extracting heat from a drain pipe. In addition, Zaloum et al. (2007) tested various forms of vertical drainage heat recovery systems and up to 27% heat recovery was achieved. Wong et al. (2010) investigated heat recovery directly from shower using a counter flow heat exchanger installed beneath the shower drain. The system was reported to achieve up to 15% heat recovery from shower water through a 1.5m. In general, the amount of energy saved from heat recovery depends on the design of the heat exchanger and the grey water generation rate. In order to increase the amount of heat recovered, researchers have investigated fitting a heat pump to the heat exchanger. Incorporating a heat pump into a grey water heat recovery system Ni et al. (2012) was able to achieve 33.9% reduction in energy consumption, whilst Baek et al. (2005) reported a 90% heat

recovery by incorporating a heat pump. However, heat exchangers have a lower cost per unit heat recovered at a given temperature range compared to heat pump and is more economical than a heat pump (Liu et al. 2014).

2.7 Summary

This chapter presents the vital areas related to this research work. Grey water has been described as domestic wastewater excluding toilet waste. It can be classified as light or dark depending on the level of contaminant, light grey water having the lowest contaminant levels. As expected, the level of contaminants in grey water varies depending on its source. Grey water sourced from the bathroom can be classed as light grey water as it consist of the lowest contaminants load. Bathroom grey water also has a high level of surfactants with varying levels of biological contaminants. Grey water sourced from clothes washing consists of moderate levels of surfactant and microorganism and can be classified as light/dark grey water. Kitchen grey water has the highest biological and organic contaminant load and is categorised as dark grey water. Due to the high contaminant load of grey water sourced from the kitchen, it is typically excluded from grey water recycling.

The fundamental part of designing a grey water recycling technology is ensuring that the treated water meets the required quality regulations. Regulatory bodies in many parts of the world have developed by-laws which outlines the treated water quality requirement. Germany appears to have the strictest regulation, requiring a COD of 7.2 mg/l in the treated grey water and only allows for unrestricted use (toilet flushing and sub-surface irrigation) on the other hand China, Japan and regions in Australia allows for a COD of 28.6 mg/l for unrestricted non-potable uses.

Graphite intercalation is the process of introducing a guest substance between the graphene layers of graphite. The resulting product is called graphite intercalation compound and several synthesis mechanisms were discussed in this chapter. The main GIC of interest is the graphite bi-sulphate form which is the method through which Nyex™ was synthesised.

The fundamentals of adsorption is also presented in this chapter. Adsorption is a very important process in this research work and the classification of adsorption isotherms and kinetics is very important in understanding the adsorption characteristics of the Nyex™ adsorbent. The pseudo-first and pseudo-second order adsorption kinetics provide some information of the adsorption reaction occurring on the adsorbent, thus defining the rate limiting step of the adsorption

process. The adsorption isotherm provides some information on the arrangement of adsorbate molecules on the surface of the adsorbent which is important in determining the optimal conditions for the adsorption process. Various design models for packed bed column has also been presented. The main step in designing a packed bed column is understanding the adsorption profile by producing a breakthrough curve experimentally. The dynamic, mass balance and scale up model described in this chapter can then be fitted to the experimental data. Successful fit of the model to the experimental data means that the model can then be used to predict breakthrough curves at various operating conditions thus enabling scale up/design of the packed bed column.

The importance of electrochemical technologies in water and wastewater treatment is highlighted in this chapter, with particular emphasis on the mechanism of electrochemical oxidation reaction. From reviewing the various mechanisms of electrochemical oxidation reaction, it was noted that both the direct and indirect reaction mechanisms involved a number of reactions taking place on the surface of the anode electrode and the bulk solution. Research work conducted to date to investigate electrochemical regeneration of GIC materials are limited to that carried out using Nyex™. The main findings from previous study have shown that electrochemical regeneration is more effective in the presence of NaCl and when a current density of 20mA/cm^2 is passed across the electrochemical cell. A review of Electrochemical disinfection from the production of ozone, hydrogen peroxide and free chlorine disinfectant revealed that although ozone and hydrogen peroxide disinfectants has a higher disinfection potential compared to free chlorine, the very short life of the latter disinfectants means disinfection can only occur on the surface of the electrode and not within the bulk of the solution. This therefore limits the overall disinfection capacities of the zone and hydrogen peroxide disinfectants.

A high proportion of energy used in the UK is used in homes rather than in industry. This therefore indicates that energy recycling in the home presents a major opportunity to cut energy usage and thus reduce cost to consumers. It has been estimated that the majority of energy used in the home is used for water heating. Various forms of heat recovery technology currently exist for mainly industrial use. Technologies for heat recovery system from grey water has recently been developed for residential use. It was concluded after reviewing the various researched methods that the most appropriate heat recovery method to consider would be the installation of a heat coil close to the grey water source to recover the heat energy through heat exchange.

CHAPTER 3:
MATERIALS AND METHODOLOGY

Overview

The experiments undertaken to achieve the objective of this project are outlined in this chapter. Studies were conducted in both batch (section 3.2.1) and continuous mode (section 3.2.2). Batch adsorption experiments were initially carried out to investigate the adsorption characteristics of Nyex™, with the aim of determining the adsorption efficiency of Nyex™. Batch electrochemical regeneration studies were also conducted to investigate regeneration of Nyex™ saturated with contaminants from grey water. Once the batch adsorption and electrochemical regeneration characteristics of the Nyex™ adsorbent were determined, the Nyex™ adsorbent was then placed in an electrochemical cell which was operated in continuous mode. The continuous adsorption and electrochemical regeneration studies were undertaken to evaluate efficiency of the electrochemical cell used in this work as well as to generate breakthrough curves/adsorption profile to aid in design. The materials and equipment used to conduct these experiments are described. Adsorption kinetics, adsorption isotherms and breakthrough data has been used to enable the most efficient process design of the Arvia™ process for grey water recycling.

3 MATERIALS AND METHODOLOGY

3.1 Materials

3.1.1 The Adsorbent (Nyex™)

Nyex™ adsorbent was supplied by Arvia™ Technology Ltd in the form of flakes (Figure 3.1). The adsorbent is a graphite intercalated compound (GIC) with a mean particle diameter of 450 µm (a more detailed description of Nyex™ can be found in chapter 2.3.5 and 2.3.5).

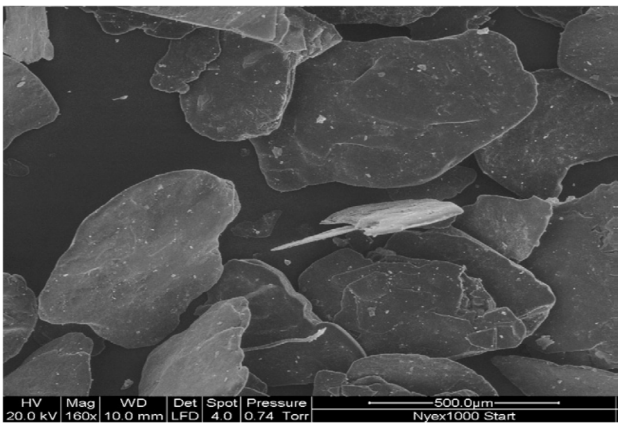


Figure 3.1 - SEM micrograph of Nyex™ adsorbent used in this study (Mohammed et al. 2011)

3.1.2 The Adsorbate (Grey Water)

Although responsible for almost 60% of the total grey water discharge, grey water sourced from the bathroom has been established to contribute to half as much, and at times less of the total pollutant load in grey water (Birks and Hills 2007; Friedler 2004). For this reason, grey water generated in the bathroom was selected as the main grey water source in this project. In order to reduce variability in the experimental conditions as well as to ensure reproducibility of data, a synthetic grey water (SGW) solution which mimicked grey water generated in the bathroom was formulated using guidelines provided by the British Standards Institution (BSI) (British Standards Institution 2011). Synthetic grey water was formulated using shower gel and sunflower oil to provide indicators for organic contaminants, septic effluent was also added to simulate biological as well as organic contaminants. Septic effluent used for SGW formulation was supplied by the Analytical Laboratory of United Utilities PLC (APPENDIX A).

3.1.3 Catholyte Solution

Catholyte solution (electrolyte) was used in the continuous adsorption and regeneration process to increase conductivity and thus reduce operating voltage. The catholyte solution was added to the cathode compartment of the electrochemical cell of the catholyte system. Catholyte solutions were made up using tap water, 3% w/v sodium chloride (NaCl) and in some case were dosed with hydrochloric acid in order to maintain the pH of the solution below 2. A 3% w/v NaCl was used in these experiments as it has been found to be an optimal electrolyte concentration for electrochemical regeneration (Brown et al. 2004b).

3.2 Equipment and Experimental Methods

3.2.1 Batch adsorption and electrochemical regeneration

Experiments conducted in batch experimental mode used a known volume of synthetic grey water (SGW) which was kept constant throughout the duration of the experiment. The experiment was conducted at room temperature which varied between 21°C and 24°C. Batch adsorption studies were carried out by mixing Nyex™ with the SGW under various conditions to determine the adsorption kinetics and adsorption isotherm. Batch regeneration studies were conducted by first saturating the Nyex™ adsorbent with the SGW and then regenerating the adsorbent using electrochemical regeneration technique.

3.2.1.1 Adsorption kinetics study

Aim

The adsorption kinetic studies consisted of an initial test to investigate the adsorption of individual contaminants in SGW onto Nyex™ over time. The main aim of this study is to determine the time taken for the system to reach equilibrium under different conditions. Adsorption kinetics studies were undertaken to help establish the type of adsorption (chemisorption or physisorption) taking place on the Nyex™.

Method

For each set of experiments, 150 ml of SGW with a known initial concentration was mixed with a known mass of Nyex™ in a 250 ml Erlenmeyer flask. The flask was then shaken at a constant speed of 260 rpm (Stuart SSL1 orbital shaker) which enabled the Nyex™ to remain in suspension, thus ensuring maximum mass transfer (Figure 3.2). Samples were collected at timed interval and were filtered using Fisher (QL110) filter paper to separate the Nyex™ particle. Filtered samples were then analysed using the appropriate analytical methods (section 3.3.1).

3.2.1.2 Adsorption isotherm study

Aim

Adsorption isotherm study was carried out in order to determine the mechanism of adsorption as well as the adsorption capacity. Resulting data from this study should aid in determining the dependency of the adsorbed phase concentration on the liquid phase concentration.

Method

Adsorption isotherms were determined by mixing 150 ml of SGW at a range of initial concentrations with known mass of Nyex™. The slurry was mixed in a 250 ml Erlenmeyer flask using a Stuart SSL1 orbital shaker at a speed of 260 ppm (Figure 3.2). The slurry was mixed for 1 hour, a time at which the system was assumed to have reached equilibrium. Samples collected after equilibrium were filtered and then analysed as discussed in section 3.3.1.

Figure 3.2 - Shaker and flask equipment used for conduction batch adsorption experiments

3.2.1.3 pH effects

During electrochemical regeneration hydrogen ions migrates to the anode and hydroxide ions to the cathode compartment of the electrochemical cell. This results in a change in pH to around 2 in the anode and 11 in the cathode compartment. Therefore, experiments were carried out at a pH range of 2 to 11 to analyse the effect of pH on adsorption. The pH of the solution was adjusted using hydrochloric acid and sodium hydroxide.

3.2.1.4 Effects of sodium chloride (NaCl)

Sodium chloride (NaCl) was added to the system during the electrochemical regeneration process in order to increase electric conductivity. Hence the effect of addition of NaCl on adsorption was investigated by preparing SGW in water containing a known concentration of NaCl. The range of NaCl concentration tested in this study was 0 to 3% w/v. In all other respect the experimental procedure was as described above for batch adsorption kinetics study.

3.2.1.5 Electrochemical regeneration

Aim

The aim of this study was to evaluate if Nyex™ adsorbent saturated with contaminants from SGW can be regenerated. The regeneration efficiency of the system was analysed by comparing the adsorption capacity of the regenerated and fresh Nyex™.

Method

To test the regeneration efficiency of the system, a batch phase electrochemical regeneration study was carried out using a sequential batch reactor (SBR). The SBR consisted of an anode and cathode compartment, separated by a micro-porous Deramic 350 membrane (Figure 3.3). The anode and cathode electrodes are both made of graphite material with an active area of 15 cm^2 for each electrode. The anode compartment holds the packed bed of adsorbent whilst the cathode compartment consists of a catholyte solution made up of 3% w/v NaCl solution. The method used for determining the regeneration efficiency was as follow:

Step 1 – *Initial adsorption*: 125 g of Nyex™ was added to the anode compartment along with a 200 ml SGW. Air was then pumped into the anode compartment to aid in the mixing of the mixture. Samples collected after equilibrium were filtered and analysed for COD and anionic surfactant.

Step 2 – *Electrochemical regeneration*: after the initial adsorption step, the air flow was stopped and the Nyex™ adsorbent was left to settle into a packed bed. A DC current in the range 0.5 – 3 A was passed across the cell over a regeneration time of 2 - 30 minutes.

Step 3 – *Re-adsorption*: the content of the anode compartment was filtered leaving just the regenerated Nyex™. 200 ml of SGW was added to the anode compartment and adsorption was carried out using the same conditions as the initial adsorption step 1. The process was repeated over 7 cycles.

The aim of this experiment was to determine if using regenerated Nyex™ adsorbent provides the same adsorption capacity as fresh adsorbent and thus is an indication of the efficiency of the electrochemical regeneration process.

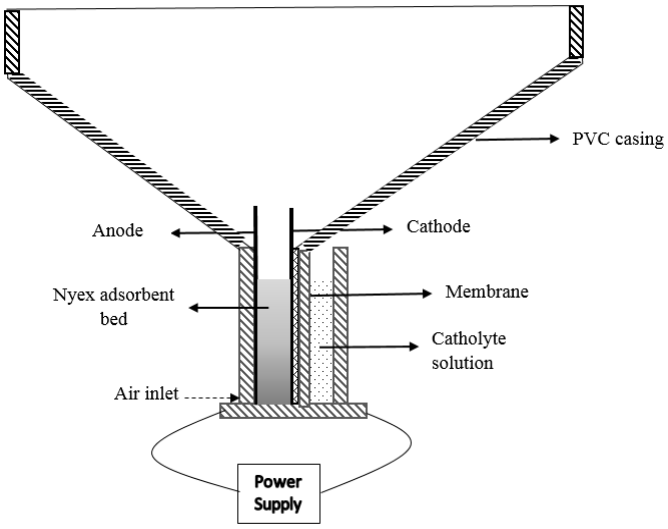


Figure 3.3 - Sequential batch reactor used for electrochemical regeneration study for Nyex™

3.2.2 Continuous adsorption and electrochemical regeneration

The effect of continuously passing an electric current across the cell on the removal of contaminants from grey water solution was investigated using an electrochemical cell (Figure 3.4 and 3.5). Electrochemical cell in the catholyte form (Figure 3.4) was initially used in this study. The catholyte based electrochemical cell was used to investigate the influence of operating parameters such as organic and hydraulic loading as well as the effect of current density. The non-catholyte system was used to investigate the impact of a sodium chloride (electrolyte) free system on treatment efficiency. The anode compartment of the catholyte electrochemical cell system was packed with enough adsorbent to cover the electrode inside the cell whilst the cathode compartment holds the catholyte (electrolyte) solution. With the non-catholyte system, Nyex™ adsorbent was placed in both the anode and cathode compartment and influent solution is pumped into both compartments. Mixing of the SGW introduced into the electrochemical cell with Nyex™ adsorbent was achieved using liquid jets generated from pumping the solution through various small nozzle/holes (Figure 3.6). The 32 (0.5 mm) holes were on a plate which was placed at the bottom of the electrochemical cell. This hole configuration was selected in this research as it had been shown based on unpublished work conducted at Arvia™ Technology to provide the optimum flow pattern for mixing.

3.2.2.1 Catholyte system

Packed bed adsorption study

This test was used as a method for investigating the effectiveness of the packed adsorbent bed within the electrochemical cell for treating SGW. Synthetic grey water of known initial concentrations was pumped at known flowrates through the bottom of the cell. Samples of the treated SGW were collected at timed intervals above the packed adsorbent bed. Samples collected were filtered and analysed. No electric current was passed across the cell during this study.

Continuous adsorption and electrochemical regeneration study

The system was operated in a continuous mode where adsorption and electrochemical regeneration occurs simultaneously. Meaning while the grey water was flowing through the adsorbent bed a DC current was passed across the cell.

During operation, SGW solution was pumped through a nozzle at the bottom of the anode compartment of the cell and allowed to flow through the packed bed. Grey water solution with

a known initial concentration was pumped through the packed bed of adsorbent at a known flowrate, current was passed continuously across the cell. Samples were collected from the top of the cell and analysed.

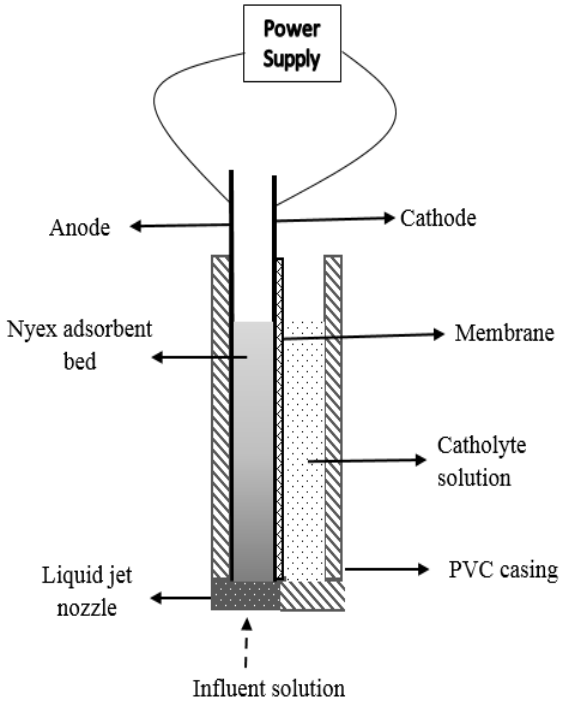


Figure 3.4 - Catholyte electrochemical cell system used for continuous adsorption and electrochemical regeneration study

3.2.2.2 Non-catholyte system

The same studies described above for the catholyte system was also carried out using the non-catholyte system. However, the non-catholyte system was mainly used to investigate the possibility of a sodium chloride free electrochemical system. In this case, a 3% w/v sodium chloride was added to the SGW solution and then pumped through both the anode and the cathode compartment of the electrochemical cell. The same test was then repeated under the same experimental condition using SGW solution with no NaCl added.

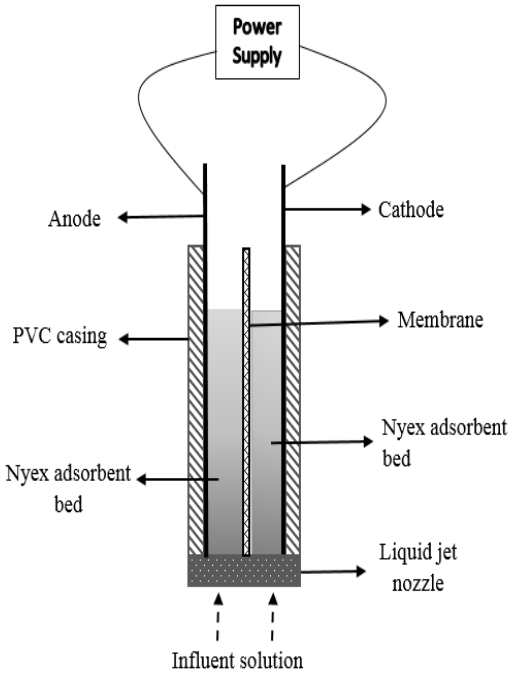


Figure 3.5 - Non-catholyte electrochemical cell system used for continuous adsorption and electrochemical regeneration study

Figure 3.6 - Top view of the 32, 5 mm hole configuration on the plate at the bottom of the electrochemical cell. This nozzle was used as a means for mixing the SGW and the Nyex™

3.2.2.3 Heat Recovery

Figure 3.7 presents a block diagram of the pilot system used for investigating heat recovery. The device consists of 2 large 250 litre polyethylene tanks, two feed pumps and a filter. Influent solution pumped from its source using pump P1 flows through the filter and then into a feed tank. Water from the feed tank was then pumped via pump P2 through the electrochemical (EC) cell with the treated solution collected in the treated water tank.

In order to investigate the possibility of heat recovery, the system was insulated throughout and water at various known temperature was pumped from the bathroom through the insulated device. Thermocouples were installed (T1 – T6) at various points around the system as indicated in Figure 3.7. The temperature of the water was recorded as it was pumped through the system.

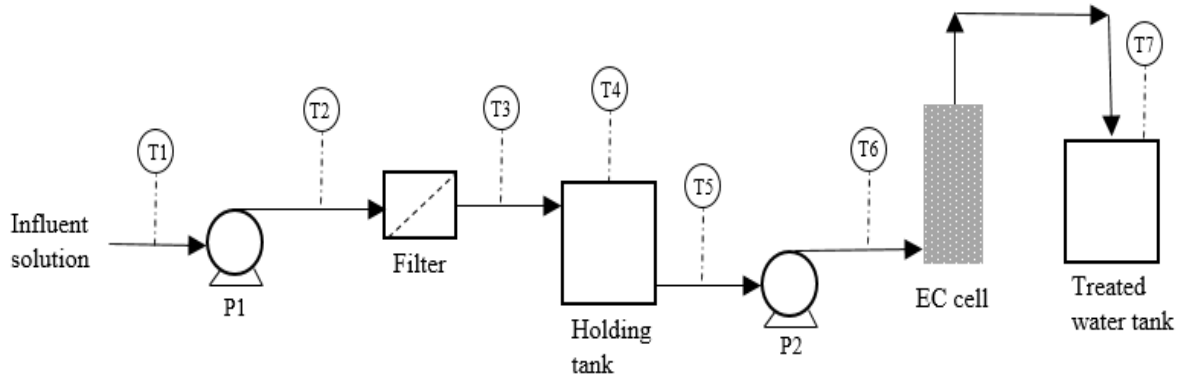


Figure 3.7 - Block diagram of grey water and energy recycling pilot rig

3.3 Analytical Methods

3.3.1 Sample Analysis

Ammonia, Nitrate, COD and anionic surfactant concentrations in the feed and treated grey water solution were determined using the Hach-Lange photometric cuvette test. Samples were initially added to the appropriate cuvette and then treated according to the manufacture's manual. The treated cuvette is subsequently placed in a Hach-Lange DR 2800 spectrometer where the absorbance of the sample was measured at wavelength of 605nm. The pH and temperature value of the samples were analysed using the Hach sensION+ MM374 pH meter. Before testing, the probe was calibrated using the appropriate buffer solutions. Biological analyses were undertaken by United Utilities PLC Laboratory, using a membrane filtration technique with a membrane lactose glucuronide agar gel incubated at 44°C. Analysis of ammonia, nitrate and anionic surfactant were also undertaken by the United Utilities Laboratory in order to verify test results obtained using the Hach-Lange photometric cuvette test method. Chlorine content in the sample solution was determined using DPD-Colorimetric method (Taylor and Phelan 2003; Palin 1957)

3.3.2 Data Analysis

3.3.2.1 Adsorption data

Solid phase concentration/ adsorbent capacity (q)

The adsorption capacity of the adsorbent (also referred to as the adsorbed phase concentration) is defined as the adsorbate mass divided by the mass of adsorbent in mg/g. It was calculated from a mass balance across the liquid and solid phases and takes the form:

$$q(t) = \left(\frac{C_0 - C(t)}{m} \right) V \qquad [3\text{-}1]$$

Where C_0 is the initial concentration in mg/l, $C(t)$ is the concentration in mg/l at time t, m is the mass of the Nyex™ adsorbent used and V is the volume in *ml* of grey water solution.

Percentage reduction

The percentage reduction in contaminant at time, t, was used to determine the treatment efficiency of the system and was estimated using the equation:

$$Treatment\ efficiency\ (\%) = \frac{C_0 - C(t)}{C_0} \qquad [3\text{-}2]$$

Linear and non-linear regression method

The least square method for linear and non-linear regression was used to fit models to experimental data. A non-linear fit of the model was determined using solver function in Microsoft Excel. Linear and non-linear fit were obtained by minimising the sum of squared errors described as:

$$SSE = \sum_{i=1}^{n} \left(q_e^{Exp} - q_e^{Mod} \right)_i^2 \qquad [3\text{-}3]$$

Where q_e^{Exp} and q_e^{Mod} are values obtained from experimental data and the model, respectively. The constants in the models were used as the adjustable parameters to minimise the error function. Correlation coefficient, R^2, representing the percentage of variability in the dependent variable, is used to analyse the fitting degree of the models with the experimental data. The correlation coefficient was calculated as:

$$R^2 = \frac{\left(q_e^{Exp} - \overline{q_e^{Mod}}\right)^2}{\sum\left(q_e^{Exp} - \overline{q_e^{Mod}}\right)^2 + \left(q_e^{Exp} - q_e^{Mod}\right)^2} \quad [3\text{-}4]$$

3.3.2.2 Electrochemical regeneration data

The efficiency of the electrochemical process was measured based on how effective charge passed across the cell is at removing a specific mass of contaminants over a certain period of time. The equations discussed below were utilised in investigating the efficiency of the electrochemical regeneration process.

Regeneration efficiency

The percentage regeneration efficiency (%RE) was estimated as a ratio between adsorption capacity of fresh and regenerated Nyex™ adsorbent. This calculation was carried out in order to investigate if the adsorbent is able to regain its full adsorption capacity after adsorption. %RE was estimated using the equation (Narbaitz and Cen 1994):

$$\%RE = \frac{q_r}{q_o} \times 100 \quad [3\text{-}5]$$

Where q_o is the initial adsorption capacity of the fresh Nyex™ adsorbent obtained from cycle 1 and q_r is the adsorption capacity of the regenerated Nyex™.

Current efficiency

The current efficiency provides a good indication of the regeneration efficiency for the continuous adsorption and regeneration process.

The current efficiency was estimated as a ratio between the theoretical charge required and the actual charge used during operation. This enabled estimation of the percentage of current passed across the cell which particpated in the regeneration of Nyex™. A low current efficiency means a high percentage of current passed across the cell is either being used up for side reactions or leaves the system without aiding in any reaction.

The theoretical charge required for the destruction of organic contaminants based on the COD value has been formulated by Comninellis and Pulgarin (1991). The formulated equation is based on the quantity of organic contaminants removed, the transfer of electrons required to

remove 1g of organic contaminants and the Faraday constant (F), it takes the form (Brown and Roberts 2007; Comninellis and Pulgarin 1991) (APPENDIX B):

$$\text{Theoretical charge required, } Q_T = \frac{(C_i - C(t))VF}{8} \quad [3\text{-}6]$$

$$\text{Actual charge used, } Q_A = It \quad [3\text{-}7]$$

Hence the current efficiency is:

$$\text{Current efficiency, } CE = \frac{(C_0 - C(t))VF}{8It} \quad [3\text{-}8]$$

Where C_0 and $C(t)$ are the initial and final concentration respectively, V is the volume passed through the cell, I is the operating current, t is the treatment time and F is the Faraday constant.

However the equation to estimate current efficiency for anionic surfactant has not been determined. The theoretical charge (Q_T) required to fully oxidise adsorbed organic contaminants can be estimated depending on the products formed during oxidation. Anionic surfactant in the form of sodium lauryl sulphate (or sodium dodecyl sulphate) can be completely oxidised as follow:

$$NaC_{12}H_{25}SO_4 + 23H_2O \rightarrow 12CO_2 + 71H^+ + Na^+ + SO_3^- + 71e^-$$

The theoretical charge (TC) can be estimating using the equation:

$$Q_T = \frac{n_e q_e F}{M_W} \quad [3\text{-}9]$$

Where F is the Faraday's constant (96487 C/mol), M_w (288 g/mol) is the molecular weight of the organic compound, qe is the adsorption capacity at equilibrium and n_e is the number of electrons required. Thus, the theoretical charge required for complete oxidation of anionic surfactant can be estimated using the following equation:

$$Q_T = \frac{71 * q_e * 96487}{288} = (2.4 * 10^4) * q_e \quad [3\text{-}10]$$

As mentioned earlier, the current efficiency (CE) is a ratio of the theoretical charge (Q_T) and actual charge (Q_A). Hence the CE based on anionic surfactant reduction can be calculated using the equation:

$$CE = \frac{Q_T}{Q_A} = \frac{(2.4*10^4)q_e}{It} \quad [3\text{-}11]$$

Where I is the current and t is the regeneration time.

3.3.3 Error analysis

The errors in the work undertaken in this study have arisen mainly from the variability in room temperature, the composition of the synthetic grey water, the pH of the tap water use to formulate the grey water, and to some extent the accuracy of the analytical methods used in the study. In order to minimise these errors and estimate the level of error relating to a given measurement, multiple trials were conducted for each measured quantities. Experiments were repeated several times until percentage relative error ($\%R_e$) is below 10%. In most cases two trials were sufficient whilst in other cases up to 4 trials was necessary.

Estimating experimental error

The experimental error was estimated by calculating the mean and the standard deviation from data obtained from measurements of a given quantity (x). The mean is defined as:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i \quad [3\text{-}12]$$

Where N is the number of measured quantity and x_i is the i_{th} measurement. The standard deviation is given by:

$$\sigma_x = \left[\frac{1}{N}\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2\right]^{1/2} \quad [3\text{-}13]$$

Error in data presented within text and tables in this report were represented using standard deviation, thus data are given in the form $\bar{x} \pm \sigma_x$.

The percentage relative error ($\%R_e$) was used to analyse the level of uncertainty in the measured quantity. It was obtained by dividing the standard deviation error by the average of the quantity and can be expressed as:

$$\%R_e = \frac{\sigma_x}{\bar{x}} \times 100 \quad [3\text{-}14]$$

CHAPTER 4:
RESULTS AND DISCUSSION

4 RESULTS AND DISCUSSION

4.1 Evaluation of the Adsorption Characteristics of Nyex™

4.1.1 Introduction

The aim of this part of the thesis is to determine if and to what extent Nyex™ adsorbent is able to adsorb contaminants from the synthetic grey water (SGW) solution. Adsorption of a specific compound occurs when the attractive forces between the compound and the adsorbent surface overcome the attractive forces between the compound and the aqueous solution (CARBTROL® Corporation 1992). There are several chemical compounds present in grey water (Eriksson et al. 2002), however, rather than analysing each individual compound, the parameters investigated in this report were limited to:

- Inorganic contaminants - in the form of chlorine and nitrogen based ammonia, phosphate and nitrate compounds.
- Organic contaminants - measured by chemical oxygen demand (COD) with specific analysis of anionic surfactants.
- Biological contaminants – analysed by measuring levels of E.coli and Pseudomonas

Adsorption of contaminants from grey water can occur through several different mechanisms depending on the polarity/solubility of the contaminant molecules and the characteristics of the adsorbent surface (Li et al. 2002).

The adsorption of contaminants from the SGW onto Nyex™ was initially investigated by mixing the SGW with Nyex™, with samples of treated SGW collected over a given period. The level of adsorption of contaminants onto Nyex™ was evaluated by measuring the reduction in the contaminant concentration in the treated samples. Once the level of adsorption was determined, studies were then conducted to determine the mechanism of adsorption using adsorption kinetics and adsorption isotherm models. Results obtained from the adsorption isotherm studies were fitted to the Langmuir and Freundlich adsorption isotherm models and the constants of these models were determined. The pseudo-first order and pseudo-second order kinetic models were also used to determine the rate controlling step of the adsorption process.

4.1.2 Adsorption of contaminants from grey water onto Nyex™

4.1.2.1 Adsorption of inorganic contaminants

In order to study the adsorption of inorganic contaminants from the SGW by Nyex™, filtered samples from the adsorption kinetic test were analysed for total chlorine, phosphate, nitrate and ammonia.

The plot in Figure 4.1 and Figure 4.2 shows the adsorption kinetics data for nitrate and ammonia respectively. It is evident from the data that Nyex™ does not remove these inorganic contaminants from the SGW. Adding Nyex™ to SGW with initial ammonia and nitrate concentrations of 0.04±0.01 mg/l and 0.7±0.15 mg/l respectively showed no substantial difference in the treated water concentration. Samples analysed for phosphorous and chlorine with initial concentrations of 3±1 mg/l and 2±0.2 mg/l respectively, also showed no adsorption onto Nyex™. This result is not surprising due to the high solubility of the inorganic contaminants investigated. Inorganic compounds are generally described as compounds without any carbon atoms and their structures are based predominantly on ionic bonding, resulting in their high solubility in water (Bansal 2010; Faust 1998). Hence, the low uptake of inorganic contaminants by Nyex™ can be explained by their high solubility in water which results in low affinity to the non-polar Nyex™ surface.

Dalahmeh (2013) reported significant removal of ammonia and phosphorous from grey water solution using two forms of adsorbent; bark and activated charcoal. However, the removal of these contaminants was thought to be accomplished through microbiological activities in biofilms generated due to the long contact time, rather than through direct adsorption onto the adsorbents.

Other researchers have also demonstrated that the adsorption of water soluble inorganic compounds onto carbon may also be attributed to the ion exchange properties of the carbon adsorbent resulting from functional groups attached to the adsorbent (Bottani and Tascón 2011; Huang et al. 2008; Le Leuch and Bandosz 2007; Asada et al. 2006; Domingo-Garcıa et al. 2002). For instance, Asada et al. (2006) investigated the uptake of ammonia by activated carbon treated with an oxidising agent in a single solute system. Results from the research illustrated that the adsorption capacity of ammonia increased as a result of acidic functional groups attached on the surface of the adsorbent. Although Nyex™ also has acidic oxygen functional

groups attached to its surface, it appears that the presence of these surface functional groups did not enable adsorption of inorganic contaminants.

Natural zeolites have proved useful for the removal of ammonia contaminants from grey water solution due to their ion exchange capabilities (Widiastuti et al 2011). A 97% removal efficiency was reported by Widiastuti et al. (2011) with electrostatic interactions being the main mechanism of removal. It is important to note that results presented in the literature highlighted above were obtained from adsorption using a single solute solution. Nyex™ adsorbent consists of acidic functional groups and these have been shown to remove ammonia in single solute solutions (Akmez Nabeerasool, Personal communication, November 28, 2013). In the case of the multi-solute grey water solutions studied here, the adsorption may have been hindered by the presence of other organic contaminants. The lack of adsorption through electrostatic interaction could also be due to the low concentration of inorganic contaminants present in the SGW solution which limits transfer of charged species from the bulk solution to the surface of the Nyex™. A summary of experimental results and data obtained in literature is depicted in Table 4.1.

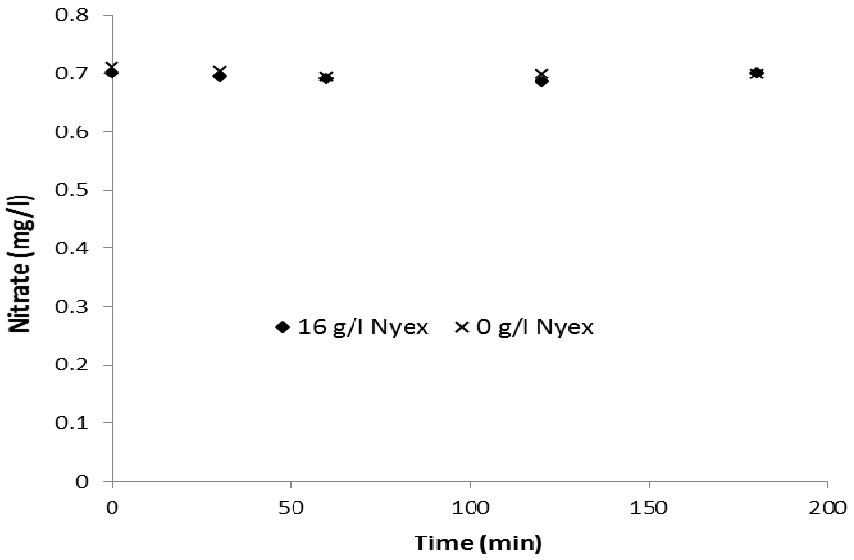


Figure 4.1 - Comparison of residual contaminant concentration in the liquid phase for treatment without Nyex™ and with 16 g/l Nyex™ over a 3 hour contact time using 150 ml synthetic grey water solution with initial nitrate concentration of 0.7±0.15 mg/l and COD concentration of 724±80 mg/l

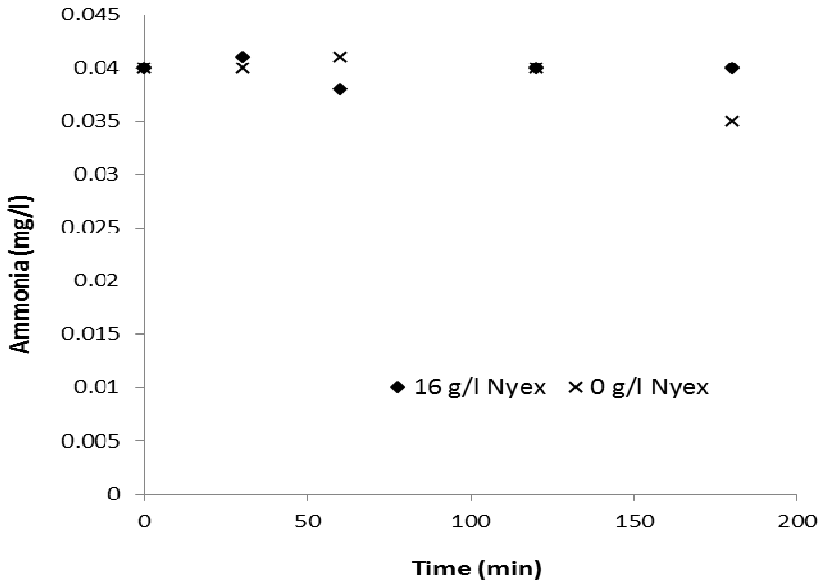


Figure 4.2 - Comparison of residual contaminant concentration in the liquid phase for treatment without Nyex™ and with 16 g/l Nyex™ for ammonia over a 3 hour contact time using 150 ml synthetic grey water solution with initial ammonia concentration of 0.04±0.01 mg/l and COD concentration of 725±50 mg/l

Table 4.1 – Comparison of experimental results with previous adsorption literature survey

Adsorbent	Results	Condition	Conclusion	Literature
Nyex	No removal of inorganics	Multisolute solution	Competitive adsorption	Experimental result
Nyex	Removal of ammonia	Single solute solution	Removal due to acidic functional group on adsorbent	Akmez Nabeersool (personal communication Nov 28 2013)
Bark and activated carbon	Removal of ammonia and phosphorous	Single solute solution	Removal through microbiological activities	Dalahmeh (2013)
Modified activated carbon	Removal of ammonia	Single solute solution	Removal through ion exchange	Asada et al. (2006)
Natural zeolites	Removal of ammonia	Single solute solution	Removal through ion exchange	Widastuti et al. (2011)
Modified coconut shell based activated carbon	Removal of ammonia	Single solute solution	Removal due to acidic functional group on adsorbent	Huang et al. (2008)

4.1.2.2 Adsorption of organic contaminants

The overall organic concentration was determined using the chemical oxygen demand (COD) test. COD values provide an indication of the capacity of oxygen required for the chemical oxidation of organic substances which can be chemically oxidized and is expressed as mass of oxygen consumed per litre of solution (mg/l).

The variations in the amount of COD adsorbed were noted in the series of contact time studied, and the results are presented in Figure 4.3. Data presented in the plot provide evidence of the uptake of organic contaminants from grey water solution by Nyex™ adsorbent. As is depicted by the drop in bulk solution concentration with an increase in Nyex™ concentration from 0 to 7 g/l. An organic contaminant removal of 20% was achieved from SGW with an initial COD concentration of 925±100 mg/l with just only 7 g/l of Nyex™.

The rapid uptake of organic contaminants noted is due to the non-polar characteristics of Nyex™ and is in accord with other findings reported for the uptake of organic contaminants in solution by Nyex™ (Asghar et al. 2014; Bouazizet al. 2014; Brown and Roberts 2013; Hussain et al. 2013; Brown et al. 2004a).

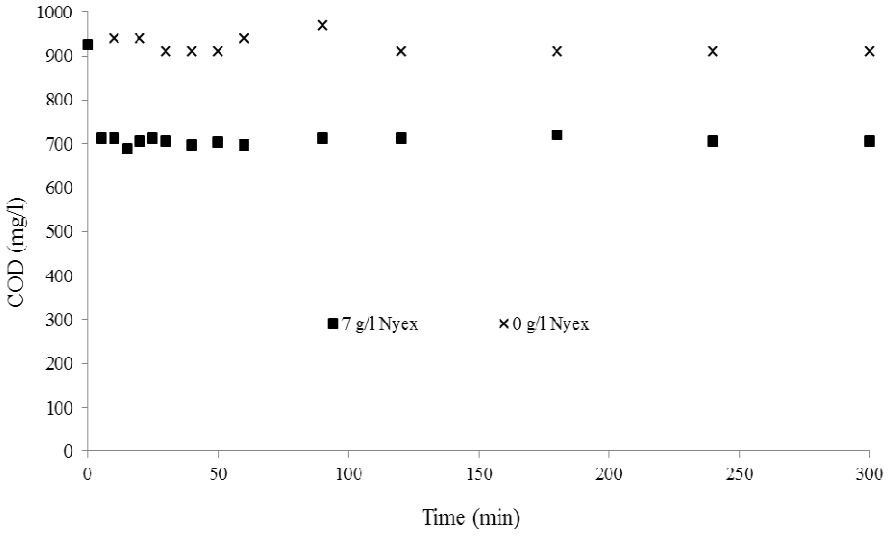


Figure 4.3 - Comparison of residual COD concentration in the liquid phase for grey water treatment without Nyex™ and with 7 g/l Nyex™ over a 5 hour contact time; test was conducted at room temperature, using 150 ml synthetic grey water solution with initial COD concentration of 925±100 mg/l

It can be seen from the shape of the curve (Figure 15.3) that adsorption of organic compounds onto the external surface of Nyex™ occurred in two stages. The first stage of which was the steeper portion where initially, with a relatively bare surface, the amount of available surface area for adsorption was high. Consequently, the initial rate of adsorption was very high and thus a rapid reduction in organic contaminants in the liquid phase was noted. The second stage was a rather constant portion with little changes in the amount of COD adsorbed due to a rapid decrease in adsorption sites. The reduction in the fraction of active adsorption sites resulted in a slower adsorption rate, which over time reached a constant value approaching equilibrium. The rate at which the majority of the active adsorption sites were occupied and thus equilibrium was achieved was very rapid, with the adsorption system approaching equilibrium in less than a minute. Rapid uptake of organic contaminants by Nyex™ has been reported by Mohammed et al. (2011) and Brown et al. (2004a) in which around 88% of the active adsorption sites were used up within the first 2 minutes.

Anionic surfactants adsorption

Surfactants are long chain organic compounds containing both hydrophilic and hydrophobic groups, which mean they contain both a water insoluble and water soluble component (Figure 4.4). The hydrophobic groups of most surfactants consist of linear, branched or aromatic hydrocarbon chain. The hydrophilic groups give the primary classification of surfactant which can be anionic, cationic, nonionic and amphoteric in nature (Figure 4.4).

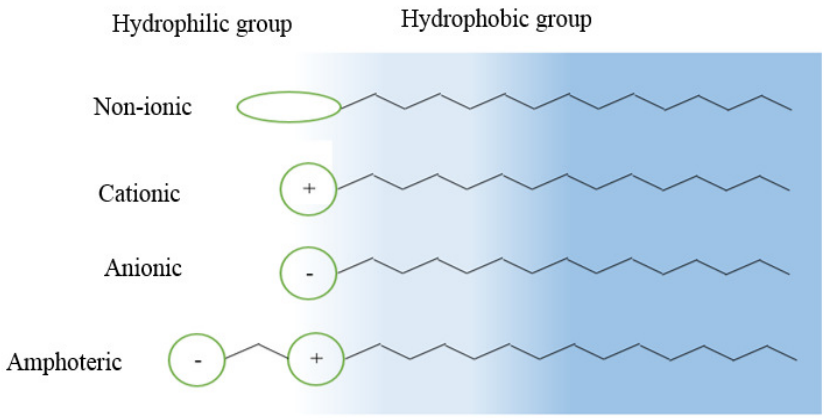


Figure 4.4 - Schematic showing the various forms of surfact, drawing attention to the polar hydrophilic group and the non-polar hydrophobic groups

Surfactants produce foam which can cause problem in the treatment process as well as affect the esthetics of the treated grey water solution. For this reason an investigation on the removal of surfactants from grey water is paramount. Of all the various forms of surfactant, anionic surfactants are more often used in household and personal care products such as shower gels. Hence, the removal of anionic surfactants was evaluated by analyzing the anionic surfactant concentration before and after treatment.

The plot in Figure 4.5 shows the adsorption of anionic surfactant onto Nyex™. This result is not surprising because anionic surfactants are organic compounds, hence precipitation from the polar aqueous solution was expected. The plot also demonstrates that adsorption of anionic surfactant onto Nyex™ was also very rapid with the majority of adsorption occurring within 5 minutes.

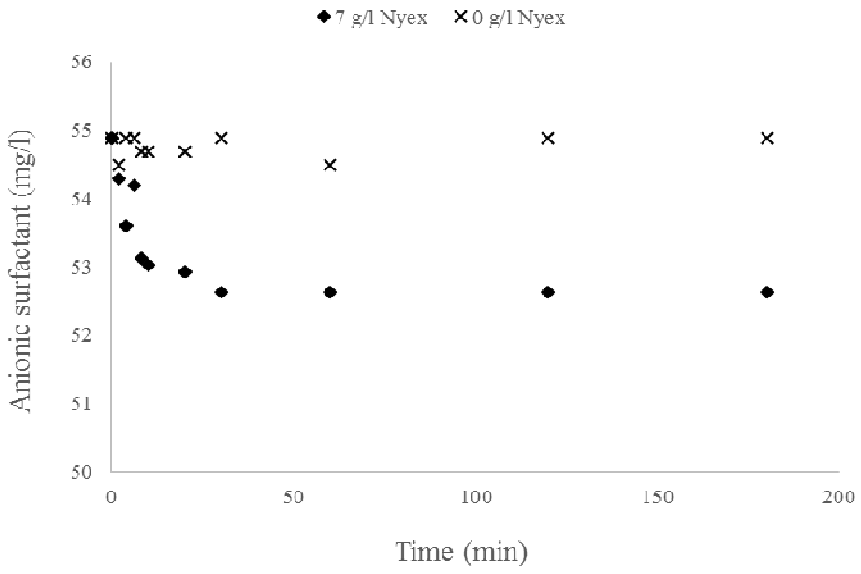


Figure 4.5 - Comparison of residual anionic surfactant in the liquid phase for treatment without Nyex™ and with 7 g/l Nyex™ for organic compounds in grey water solution over a 3 hour contact time; test was conducted at room temperature, using 150 ml SGW with an initial anionic surfactant concentration of 55±10 mg/l

A percentage anionic surfactant removal of 4% was achieved with 7 g/l Nyex™ from an initial anionic surfactant concentration of 55±10 mg/l. Purakayastha et al. (2005) reported a percentage removal of 96% for anionic surfactant using 5 g/l granular activated carbon (GAC) adsorbent at an initial anionic surfactant concentration of 2 mg/l and a 7 hour contact time. Zor

(2004) also reported high percentage reduction in anionic surfactant of up to 94% using 1 g/l activated carbon adsorbent with an initial anionic surfactant concentration of 15 mg/l.

Both Purakayastha et al. (2005) and Zor (2004) utilised single solute solution in their research work. Therefore, the low adsorption capacity experienced by Nyex™ for anionic surfactant could be as a result of competitive adsorption in the presence of other organic compounds. It could also be due to the high adsorption capacity of GAC compared to Nyex™. Further investigation on the adsorption mechanism of Nyex™ should be able to provide greater insight and is discussed in section 4.1.3.

4.1.2.3 Adsorption of biological contaminants

The ability of Nyex™ to adsorb biological contaminates was investigated by analyzing the concentration of E.coli and Pseudomonas present in samples collected from the adsorption kinetics study. Result depicted in Figure 4.6 and Figure 4.7 shows that adding Nyex™ to the grey water solution did not result in any changes compared to the blank test run. This therefore means Nyex™ adsorbent did not adsorb both E.coli and Pseudomonas from the SGW.

Although very limited, there have been some investigation on the uptake of E.coli by Nyex™ (Hussain et al. 2012; Brown et al. 2008). Tests conducted by Brown et al. (2008) showed adsorption of E.coli by Nyex™ with up to 4-Log removal achieved and with an uptake rate similar to that depicted by the uptake of organic contaminants. Although the experimental method utilized by Brown et al. (2008) was similar to that used in this project, the solution was a single solute solution spiked only with E.coli C600 and using 40 g/l of Nyex™. In the case of this project, biological contaminants such as E.coli and Pseudomonas were introduced into the SGW by spiking with sludge from wastewater treatment works which also contained organic contaminants. The lack of biological adsorption by Nyex™ could again be due to the presence of organic molecules which have more affinity towards the surface of the Nyex™ adsorbent. There was a reduction of microorganisms (E.coli and Pseudomonas), with a 0.1-log reduction noted for trials undertake with and without Nyex™. This indicates disinfection by residual chlorine in the tap water used to formulate the SGW. Further study is therefore desirable to determine the mechanism by which microorganisms are removed from grey water (section 4.1.3).

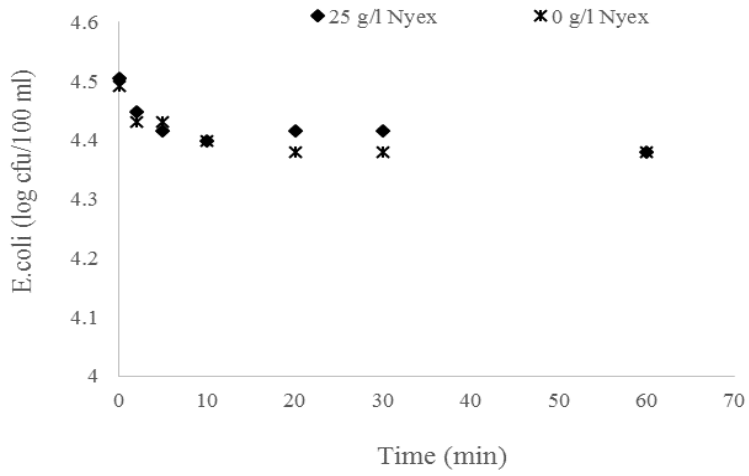


Figure 4.6 - Comparison of adsorption residual E.coli concentration in the liquid phase, for treatment conducted without Nyex™ and with 16 g/l Nyex™ over a 1 hour contact time, using 150 ml synthetic grey water solution with initial concentrations of 10^4cfu/100 ml and COD concentration of 724±80 mg/l

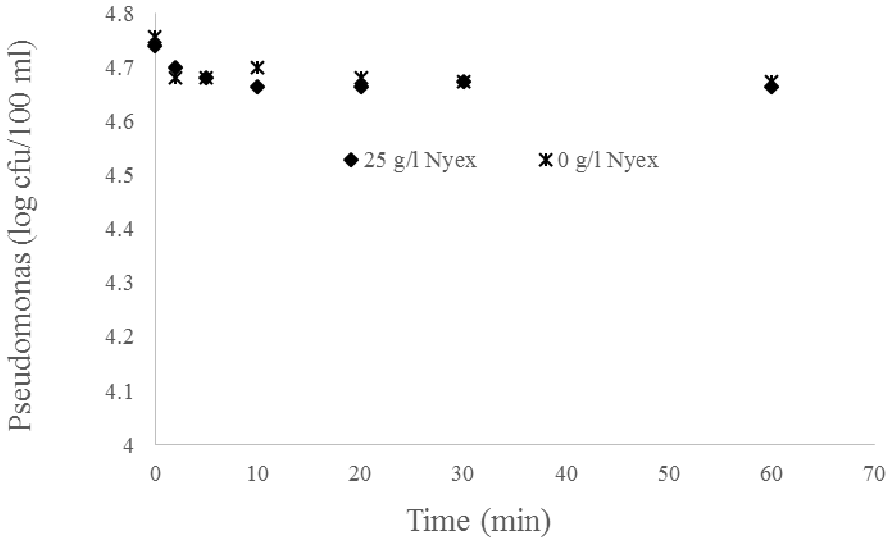


Figure 4.7 - Comparison of adsorption residual Pseudomonas concentration in the liquid phase, for treatment conducted without Nyex™ and with 16 g/l Nyex™ over a 1 hour contact time, using 150 ml synthetic grey water solution with initial concentrations of 10^4cfu/100 ml and COD concentration of 724±80 mg/l

4.1.3 Evaluation of the mechanism and type of adsorption

4.1.3.1 Factors affecting adsorption

Initial concentration (organic load)

One of the concerns highlighted from the use of several different grey water treatment processes is the variability of influent grey water concentration. This has been found to have detrimental effects on the treatment efficiency especially on biological treatment processes (Ward 2000; Šostar-Turk et al. 2005; Lin et al. 2005; Eriksson et al. 2009). For this reason the effect of organic contaminant loading on treatment efficiency was investigated over a period of time. The experimental method was similar to the method discussed in section 3.2.1. Grey water solution between the ranges of 0 to 925 mg/l was studied using 16 g/l Nyex™ adsorbent.

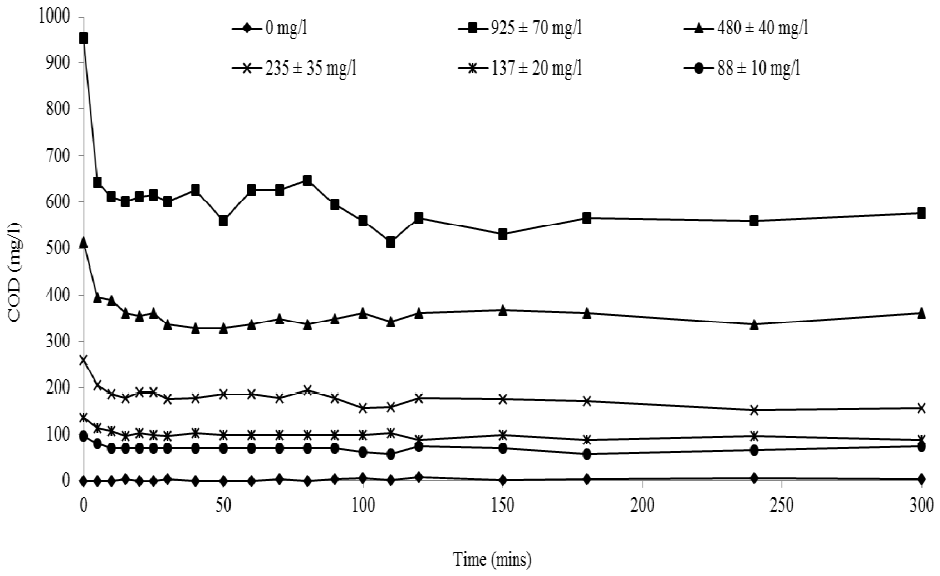


Figure 4.8 - Residual COD concentration in the liquid phase over time illustrating the effect of contact time and initial concentration on uptake of organic contaminants by Nyex™ at initial grey water concentrations between 0 mg/l and 925 ± 100 mg/l, experiment carried out in batch mode using 16 g/l Nyex™ adsorbent and 150 ml of grey water solution

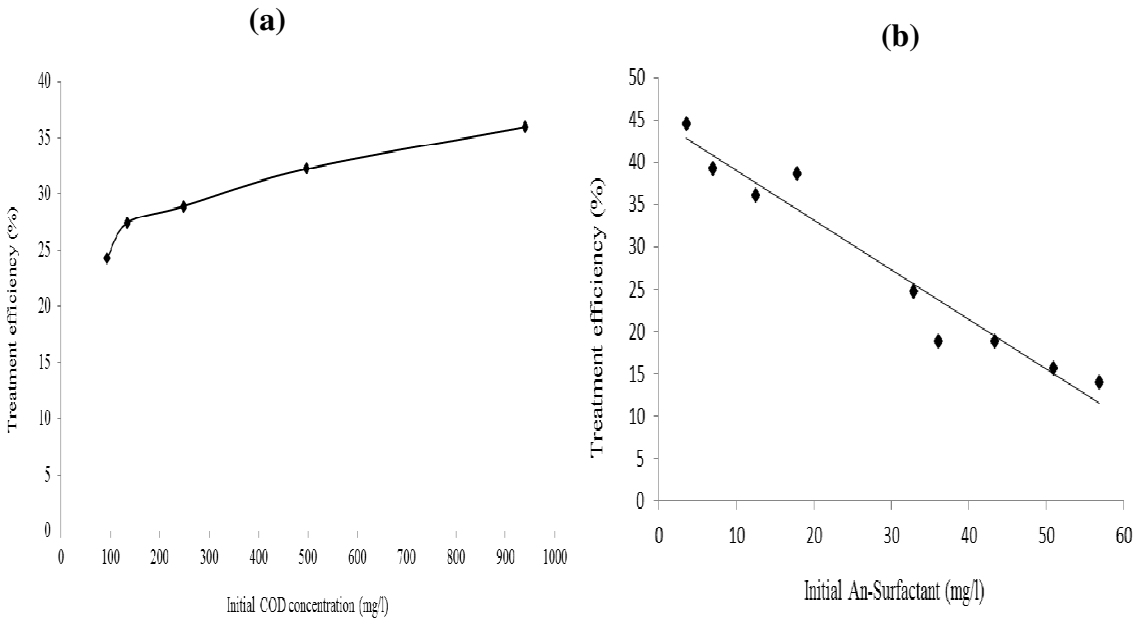


Figure 4.9 - Effect of initial grey water concentration on percentage removal of organic contaminants based on (a) COD values and (b) anionic surfactant values, experiment carried out in batch mode using 16 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

Figure 4.8 depicts the adsorption kinetics over a five hour contact time at room temperature. The initial rapid decrease in organic contaminants observed was due to a high availability of active adsorption surface at the beginning of the process. Above an initial COD concentration of 480 mg/l, the majority of the adsorption sites were occupied within a minute while at lower concentrations a contact time of 5 to 10 minutes was required. The fast initial removal rate experienced at high initial organic concentration was as a result of higher concentration difference between the concentration of contaminant in the adsorbed phase and the bulk liquid phase. The concentration difference is the primary driving force for adsorption (Boyd et al. 1947).

Figure 4.9 reveals that the amount of organic contaminants removed from the bulk grey water solution was affected by the initial grey water concentration. A 40% increase in removal efficiency was observed for COD as the initial COD concentration increased from 88 to 925 mg/l. However, in the case of anionic surfactant the treatment efficiency decreased as the initial concentration increased. This implies that adsorption of anionic surfactant molecules is dependent on the availability of active adsorption sites rather than intermolecular attraction.

Nyex™ dosage (variation of surface area)

To determine the effect of adsorbent surface area on the uptake of organic contaminants, batch experiments were performed using adsorbent concentration between 0 and 350 g/l. Adsorbent of known mass was placed in a 250 ml flask along with 150ml of synthetic grey water solution. The flask was then shaken for an hour using an orbital shaker to ensure equilibrium. The experimental method and sample analysis were similar to the adsorption isotherm experiment, but in this case, the initial adsorbent concentration was varied whilst the grey water concentration was kept constant at 724±80 mg/l.

Due to the increased adsorption surface area brought about by increased Nyex™ loading, it was expected that the total uptake of contaminants by Nyex™ should increase as the Nyex™ dosing increased. As expected, the plot in Figure 4.10 shows that increasing the concentration of adsorbent from 7 to 350 g/l did result in a higher uptake of organic contaminants by Nyex™ with a percentage increase from around 20% to 0ver 70% for COD. An interesting observation was that at adsorbent concentrations above approximately 150 g/l the plot starts to concave towards the concentration axis especially for COD adsorption as a result of reduction in percentage removal with increase in Nyex™ adsorbent dosage above this value.

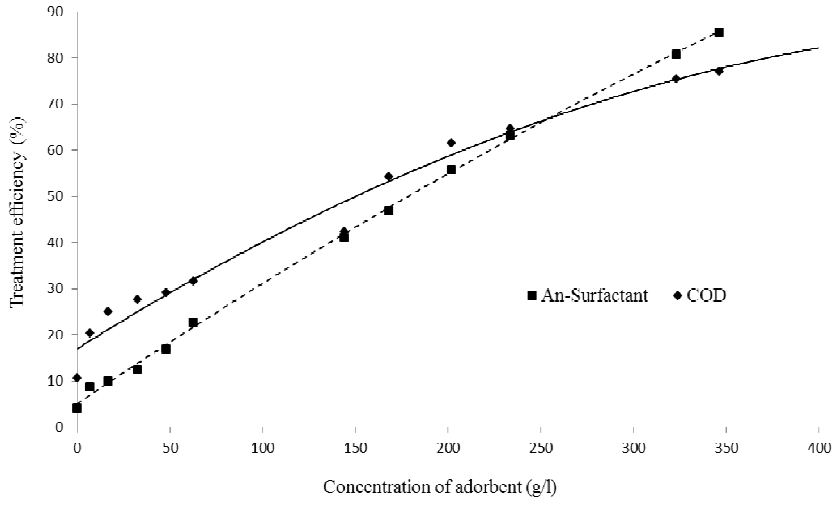


Figure 4.10 - Effect of adsorbent mass on the reduction of surfactant and COD in the liquid phase; batch experiment was performed with initial COD and surfactant concentrations of 724±80 mg/l and 50±10 mg/l respectively over a contact time of 1 hour, concentration of Nyex™ between 0 g/l and 350 g/l was studied

The reduction in percentage COD removed with increase adsorbent concentration could be due to over lapping or coagulation of the adsorbent particles at high concentration thus reducing the amount of available adsorption sites (Aroua et al. 2008).

The effect of coagulation or over lapping at high adsorbent concentration can be reduced by increased mixing of the adsorbent and grey water slurry. The effect of agitation speed was investigated by Aroua et al. (2008) on the kinetics of lead(II) adsorption onto palm shell-based activated carbon. The author concluded that increasing the agitation speed results in an increased adsorption capacity due to improved distribution of the adsorbate in the bulk liquid phase and the reduction in the film boundary layer surrounding the adsorbent.

Figure 4.10 also shows that compared to the amount of COD adsorbed, the percentage uptake of anionic surfactant adsorbed increased almost linearly from around 10% at 7 g/l Nyex™ loading to almost 90% at 350 g/l Nyex™ loading. This means that at a Nyex™ loading of 350 g/l the percentage removal of anionic surfactant was 20% more than the percentage removal for COD value. This suggests that the reduction in overall organic adsorption leaves more active adsorption sites for anionic surfactant. In order to investigate this further the data was expressed in terms of the solid/adsorbed phase concentration (adsorption capacity) (Figure 4.11 and Figure 4.12).

Figure 15.11 and Figure 15.12 shows a reduction in the adsorbed phase concentration of organic contaminants on the Nyex™. The adsorbed phase decreased from approximately 24 mg/l to 1.2 mg/l and 0.74 mg/l to 0.1 mg/l for COD and anionic surfactant respectively, with an increase in Nyex™ adsorbent concentration from 7 g/l to 350 g/l. Similar results have been observed by Brown and Roberts (2007) for the adsorption of organics from solution using Nyex™ adsorbent. The reduction in adsorption capacity can be attributed to adsorption sites remaining unsaturated as the surface area increased and the contaminant load remained the same (Garg et al. 2004). Another possible reason for the reduction in adsorbed phase concentration could be as a result of a shift in the concentration difference in the system, and thus the adsorption driving force. The fact that the adsorbed phase concentration decreased at high adsorbent loading supports the previous assumption that the reduction in overall organic contaminants leaves more active adsorption sites for anionic surfactant molecules.

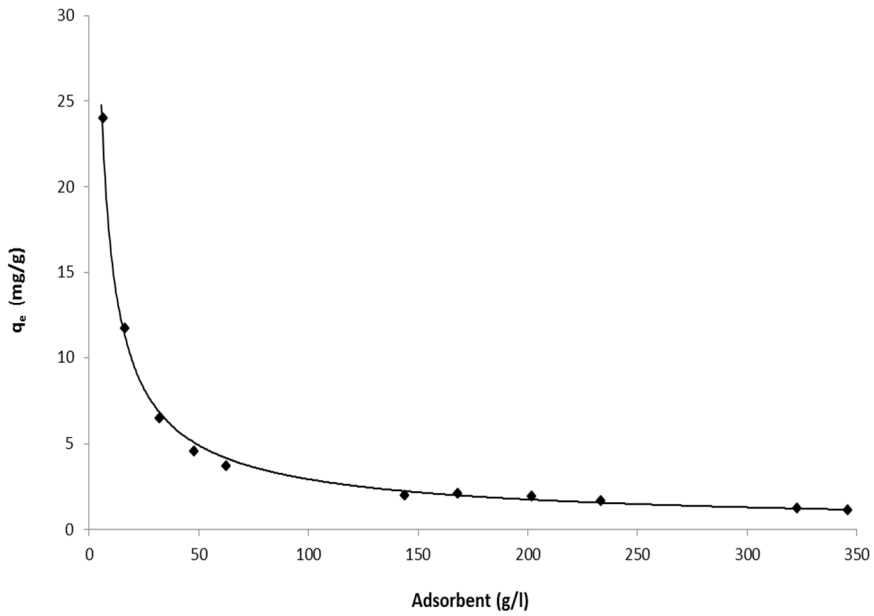


Figure 4.11 - Effect of adsorbent concentration on the adsorption capacity for COD: batch experiment was performed with initial COD and surfactant concentration of 724±80 mg/l over a contact time of 1 hour, concentration of Nyex™ between 0 g/l and 350 g/l was studied

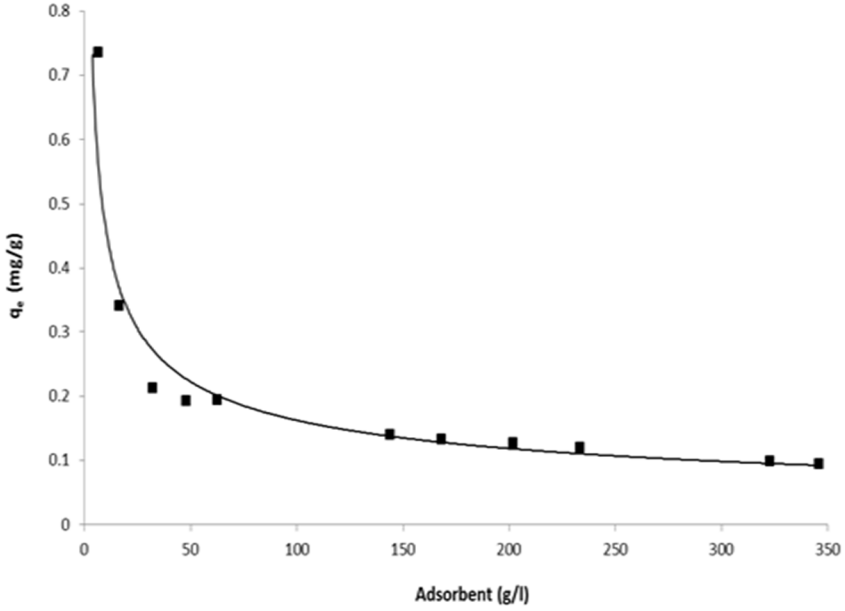


Figure 4.12 - Effect of adsorbent concentration on the adsorption capacity for anionic surfactant: batch experiment was performed with initial anionic surfactant concentration of 50±10 mg/l respectively over a contact time of 1 hour, concentration of Nyex™ between 0 g/l and 350 g/l was studied

pH of the SGW solution

The influence of pH on the adsorption of organic contaminants was investigated by varying the initial pH of the grey water solution. The pH was varied between 2 and 11 by spiking the grey water solution with 1 M of hydrochloric acid and 1 M of sodium hydroxide until the required pH was obtained. In order to evaluate the uptake of contaminants at various pH, the adsorption capacity was analysed and plotted in Figure 4.13. It can be seen from the plot that the adsorption capacity was independent of pH above pH 4 for both COD and anionic surfactants. The rise in adsorption below pH 4 suggests an increased deposition of positively charged hydrogen ions (H+) on the surface of the adsorbent at low pH (Malik 2004) resulted in a higher affinity of negatively charged anionic organic compounds to the adsorbent. Increasing the pH resulted in an increase in the amount of negatively charged hydroxide ions (OH-) and depletion of hydrogen ions (Malik 2004). There was very little change in the adsorption capacity for COD above pH 4 which suggests that the increased amount of OH- present above this pH had negligible effect on the overall adsorption of organic contaminants. On the other hand, increase in the amount of OH- on the adsorbent surface did not favour adsorption of anionic surfactants as indicated by the slight decrease in the uptake of anionic surfactant molecules (Figure 4.14). This is due to increased electrostatic repulsion between anionic surfactant molecules and OH- ions.

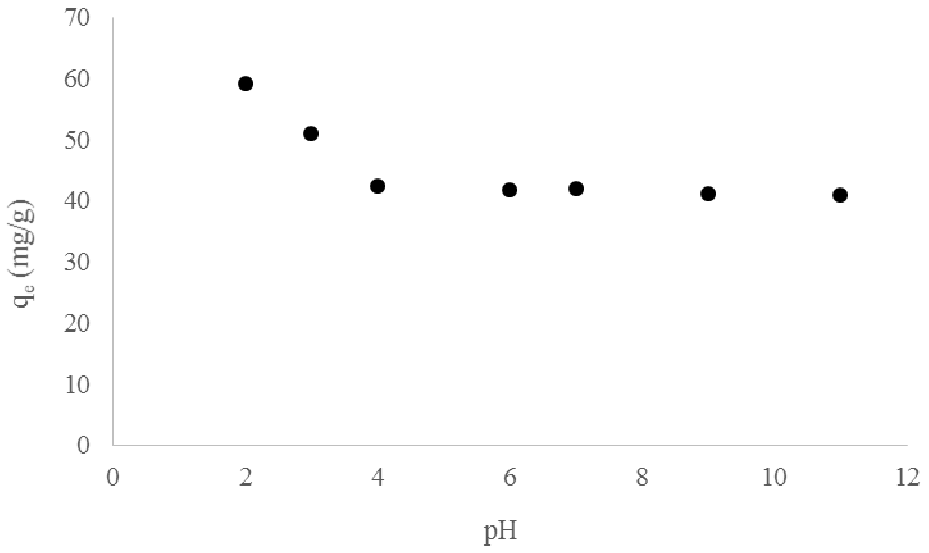


Figure 4.13 - Effect of grey water solution pH on concentration of organic contaminants in the adsorbed phase; batch experiment was performed with initial COD concentration of 925±100 mg/l with Nyex™ concentration of 16 g/l

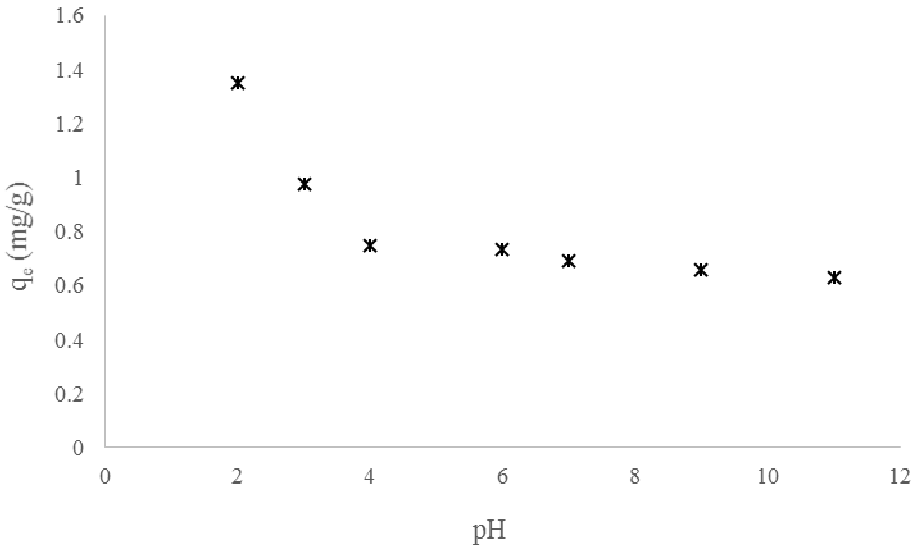


Figure 4.14 - Effect of grey water solution pH on the concentration of anionic surfactant in the adsorbed phase; batch experiment was performed with initial anionic surfactant concentration of 55±10 mg/l with Nyex™ concentration of 16 g/l

Solution salinity

The solubility of ionic (inorganic) salts in water is normally higher than that of organic molecules due to their polar nature. Hence, when ionic salts are in an aqueous solution with organic molecules, competition between these compounds to interact with water molecules often leads to an increase in adsorption of organic molecules (Bansode 2002; Noyes 1994). This is due to stronger attraction between the adsorbent and organic molecules which in turn decrease the interaction between water and organic molecules. Because an ionic salt, NaCl, is used in the Arvia™ system, its effect at a range of concentrations (0 to 3% w/v) on the adsorption of organic contaminants from SGW solution has been studied.

The influence of ionic strength on the amount of organic contaminants adsorbed is depicted in Figure 4.15 and Figure 4.16 for COD and anionic surfactants respectively. It is evident from the plot that increasing the ionic strength of the grey water solution did not have a significant effect on adsorption. There was a very small increase of less than 5% noted in the adsorption of anionic surfactant, but hardly any change observed in the overall adsorption of organic contaminants (COD). Hence, increasing interaction between highly soluble electrolyte ions with the aqueous solution did not result in a significant change in the solubility of organic contaminant molecules in the grey water solution. This overall behaviour suggests weak

interaction between water molecules and organic contaminants present in the grey water solution.

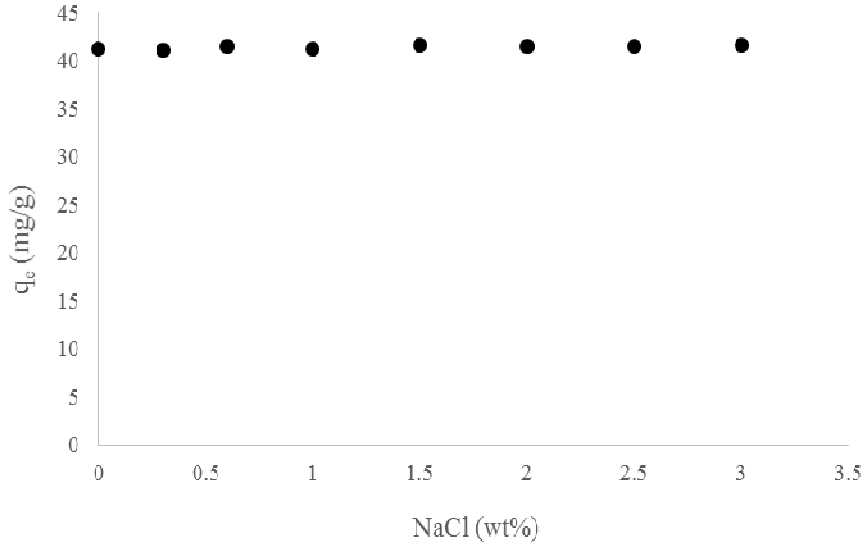


Figure 4.15 - Effect of NaCl concentration on the adsorbed phase concentration of organic contaminants; batch experiment was performed with initial COD concentration of 925±100 mg/l with Nyex™ concentration of 16 g/l

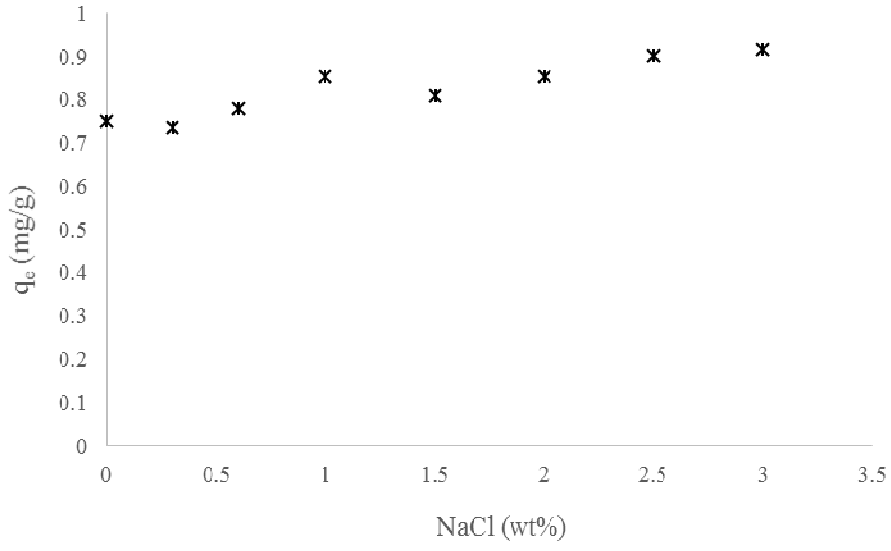


Figure 4.16 - Effect of NaCl concentration on the adsorption of anionic surfactants; batch experiment was performed with initial anionic surfactant concentration of 55±10 mg/l with Nyex™ concentration of 16 g/l

4.1.3.2 Competitive adsorption of organic compounds

Nyex™ is a low surface area non porous adsorbent and therefore has a limited active surface area onto which organic molecules can adsorb. The presence of different organic contaminants in the SGW results in competition for active adsorption sites. Different organic molecules may well have varying affinity for certain adsorption sites on the adsorbent surface and hence not all organic molecules would compete for exactly the same sites. Although there will be second order competition arising from the presence of other organic molecules. It has been noted from previous results in this study that the adsorption of anionic surfactants is lower compared to the overall organic contaminants (COD). Hence competitive adsorption was investigated by removing other competing organic contaminants from the SGW.

In this case, the synthetic grey water solution was formulated using only sodium laureate sulphate (SLS). 15 g/l of SLS flakes was used to make up a solution with an initial anionic surfactant concentration of 50±10 mg/l. The SGW was mixed with 7 g/l adsorbent and samples collected at timed interval. It is evident from Figure 4.17 that removing other competing organic compounds from the SGW resulted in an increase in the adsorption of anionic surfactant molecules. The maximum adsorbed phase concentration of anionic surfactant molecules increased from 0.4 mg/g to 2 mg/g when grey water made up of only SLS was used, that is a 40% increase in adsorption. It was also observed that the rate of adsorption remained relatively the same for adsorption studies conducted using both grey water and SLS solution.

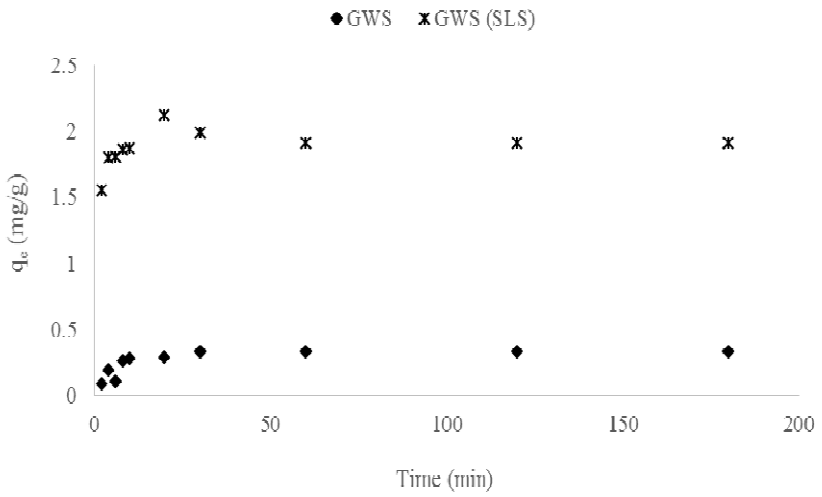


Figure 4.17 - Investigation of competitive adsorption between anionic surfactants and other organic contaminants present in grey water solution; test was conducted using the normal formulated grey water solution (SGW) and a solution made up of SLS in tap water (initial anionic surfactant concentration was 50±10 mg/l)

4.1.3.3 Adsorption kinetics model

Adsorption kinetics study was conducted in batch experimental mode using 7 g/l of adsorbent to treat SGW with a COD concentration of 925±100 mg/l.

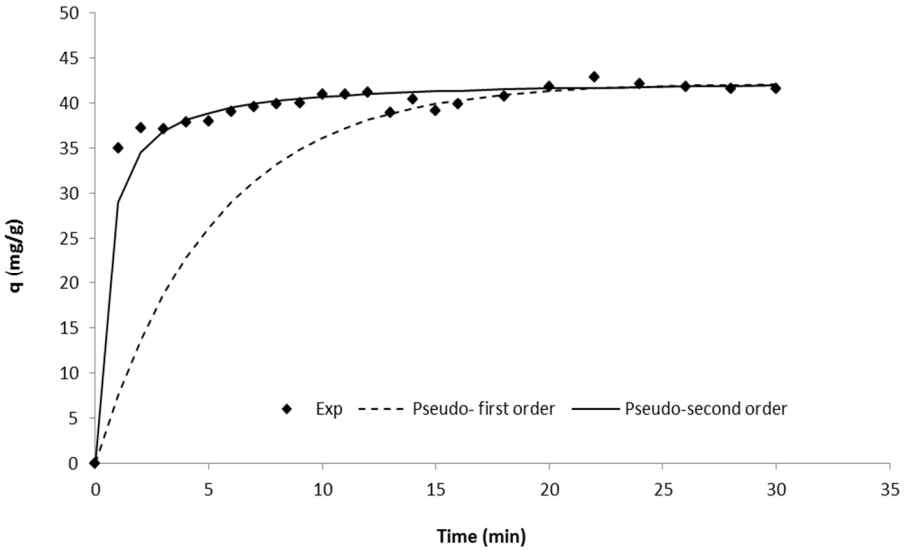


Figure 4.18 - Adsorption kinetics: non-linear pseudo-first order and pseudo-second order kinetic fit to experimental data with initial COD concentration of 925±100 mg/l using 7 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

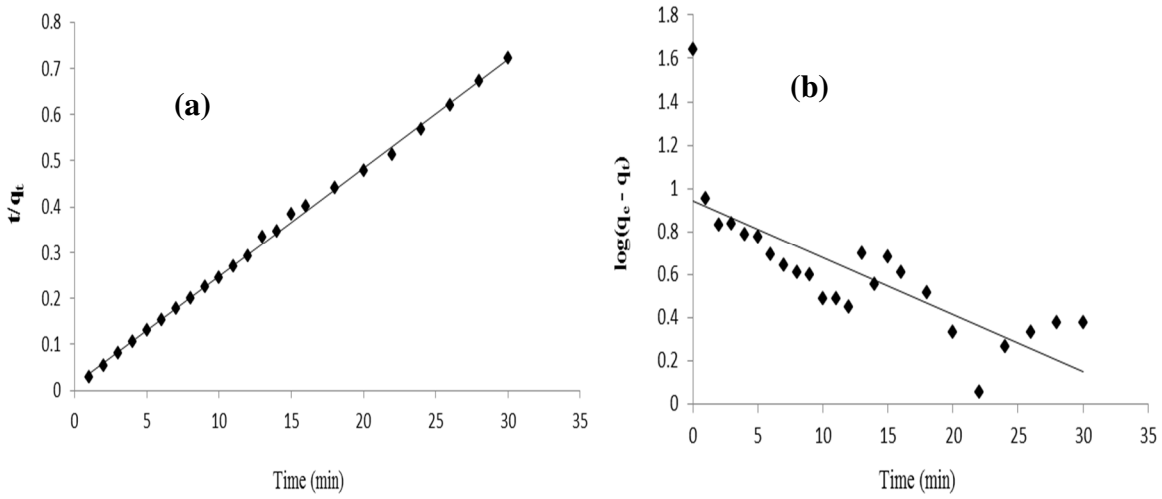


Figure 4.19 - Adsorption kinetics: linear (a) pseudo-second order and (b) pseudo-first order kinetic fit to experimental data with initial COD concentration of 925±100 mg/l using 7 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

In order to determine the rate limiting step of the adsorption, kinetic models were fitted to the experimental data. The pseudo-first order and pseudo-second order kinetic models were applied to evaluate the batch experiment data using a linear and non-linear regression fit. The correlation coefficient value R^2 was used to determine the goodness of fit. The estimated adsorption capacity at equilibrium for the pseudo-first order kinetic model was obtained by trial and error in order to acquire the highest correlation coefficient value.

Table 4.2 - Pseudo-first order and pseudo-second order parameters obtained from fitting the kinetics models to experimental data for COD, test was carried out with initial COD concentration of 925±100 mg/l using 7 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

	Pseudo-first order			**Pseudo-second order**		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
Linear	0.06	10	0.548	0.05	41.7	0.997
Non-linear	0.19	42.2	0.51	0.05	42.6	0.96

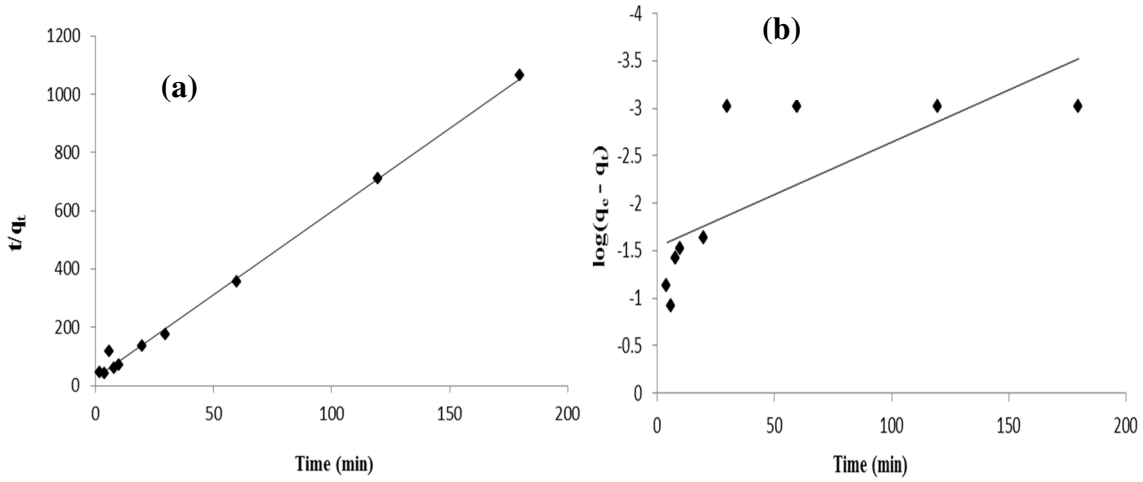


Figure 4.20 - Adsorption kinetics: linear (a) pseudo-second order and (b) pseudo-first order kinetic fit to experimental data with initial anionic surfactant concentration of 55±10 mg/l using 7 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

Table 4.3 - Pseudo-first order and pseudo-second order parameters obtained from fitting the kinetics models to experimental data for anionic surfactant, test was carried out with initial anionic surfactant concentration of 55±10 mg/l using 7 g/l Nyex™ adsorbent and 150 ml of synthetic grey water

	Pseudo-first order			**Pseudo-second order**		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min)	q_e (mg/g)	R^2
Linear	0.025	0.032	0.55	0.9	0.21	0.996

The plot depicted in Figure 4.18 and Figure 4.19 indicates that the pseudo-first order kinetic model does not correlate very well with the experimental data over the 30 minutes time period studied, in both the linear and non-linear fit. The plot in Figure 4.20 also implies that the pseudo-first order kinetic model did not correlate very well with the experimental data for anionic surfactant. This suggests that the pseudo-first order model is not a good representation of the adsorption process. On the other hand, good correlation was observed with the pseudo-second order kinetic model with a linear regression correlation coefficient value R^2 of over 0.997 (Table 4.2) for COD and 0.996 (Table 4.3) for anionic surfactant. A second order fit of the experimental data means that the adsorption rate of the system is proportional to the concentration squared. This supports the shape of the data observed in Figure 4.3, Figure 4.5 and Figure 4.8 where initially, at a higher initial concentration, the adsorption rate was very rapid.

The pseudo-second order fit of the kinetic experiment data also indicates the rate limiting step of the adsorption process is predominantly the chemical adsorption step. A pseudo-second order fit was also reported for adsorption of organic contaminants from wastewater onto Nyex™ (Mohammed et al. 2011). The estimated adsorption capacity for the initial concentration studied was 41.7 mg/g for COD and 0.21 mg/l for anionic surfactant. The second order adsorption kinetics constant was estimated at 0.05 g/mg min for an initial COD concentration of around 925±100 mg/l (Table 4.2).

4.1.3.4 Adsorption isotherm model

The adsorption curve depicted in Figure 4.21 represents a Type II isotherm for multilayer adsorption (Brunauer*et al.* 1940). The adsorption isotherm shows a steep increase in solid phase equilibrium concentration (q_e) at COD concentrations below 100 mg/l until the majority/all of the active adsorption site has been occupied. This corresponds to a monolayer adsorption in which the contaminants bind strongly to the surface of the adsorbent.

At COD concentration above 100 mg/l, no further adsorption took place after the entire active adsorption site was used up. This resulted in an increase in the liquid phase equilibrium concentration (C_e) with very little changes to q_e. There was another rapid increase in q_e at COD concentration above 230 mg/l which suggests multilayer adsorption of contaminants at high grey water concentration. Multilayer adsorption occurs as a result of adsorbed organic molecules attracting other organic molecules from the bulk liquid phase, which leads to self-association of organic molecules on the Nyex™ due to intermolecular attraction. The fact that a higher concentration is required in order to achieve multilayer adsorption implies that a high concentration gradient between the adsorbed and bulk liquid phase is required for stronger intermolecular attraction.

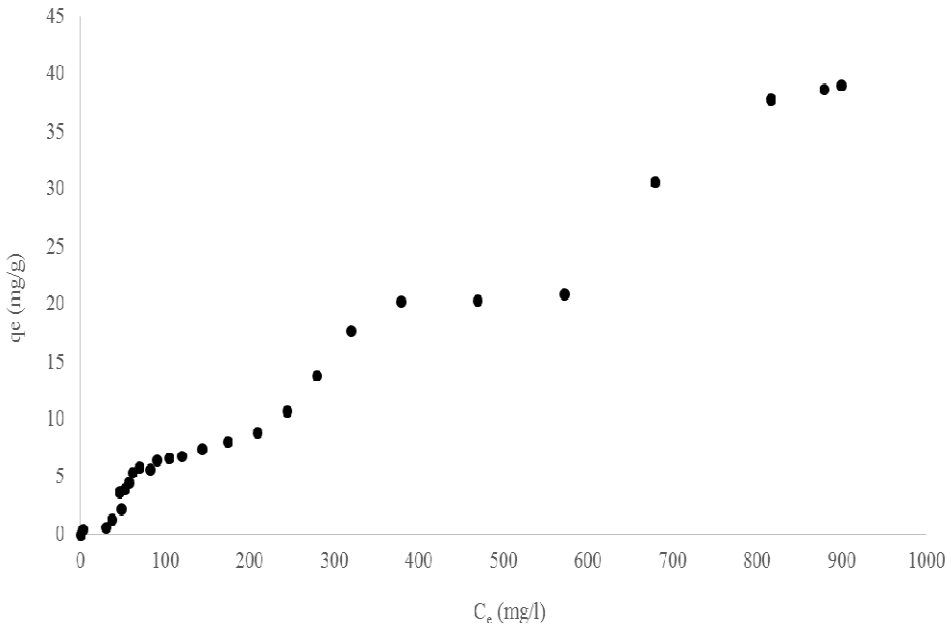


Figure 4.21 - Adsorption Isotherm result for organic COD removal carried out over a contact time of 1 hour with 7 g/l adsorbent and 150 ml synthetic grey water solution

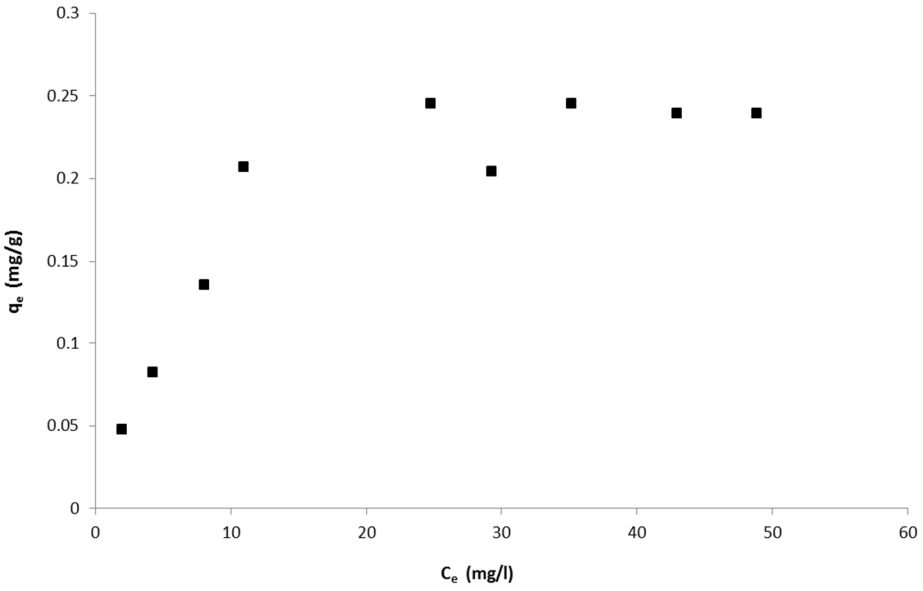


Figure 4.22 - Adsorption Isotherm result for anionic surfactant removal carried out over a contact time of 1 hour with 16 g/l adsorbent and 150 ml synthetic grey water solution

On the other hand, the adsorption isotherm curve for anionic surfactant (Figure 4.22) shows an initial rapid uptake by the adsorbent, after which the curve levels off as the system approaches equilibrium. The shape is similar to that observed at low concentration of COD in Figure 4.21, but there seem to be no evidence of multilayer adsorption of anionic surfactant over the

concentration range studied. This explains formation of monolayers on the Nyex™ adsorbent, which could be due to the fact that the non-polar hydrocarbon (hydrophobic) tail adsorbs to the Nyex™ whilst the free anionic (hydrophilic) head has a stronger affinity to water molecules than other surfactant molecules. This finding supports the data presented in Figure 4.9 where the percentage reduction of organic contaminants increased with an increase in initial concentration for COD values. Whilst for anionic surfactant increasing the initial concentration led to a reduction in the percentage removal as the molecular interaction between molecules in the solid/adsorbed phase and the bulk liquid phase is negligible.

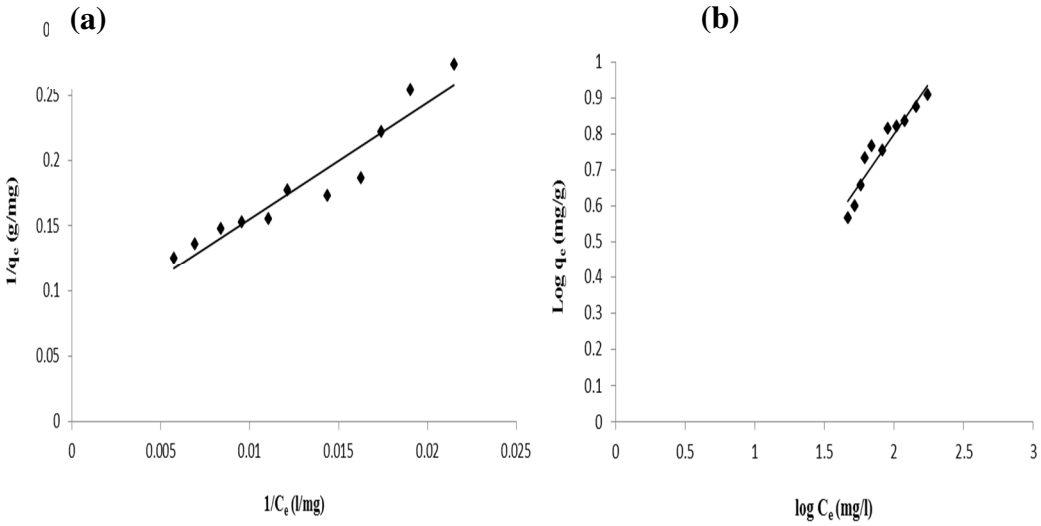


Figure 4.23 - Adsorption isotherm: linear (a) Langmuir isotherm and (b) Freundlich isotherm fit to experimental data for COD, test was carried over a contact time of 1 hour using 150 ml synthetic grey water solution

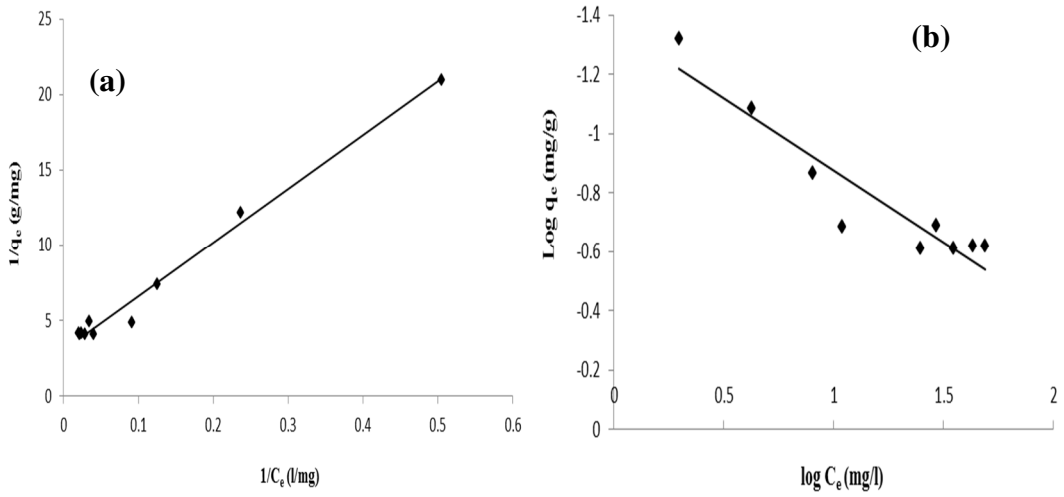


Figure 4.24 - Adsorption isotherm: linear (a) Langmuir isotherm and (b) Freundlich isotherm fit to experimental data for anionic surfactant, test was carried over a contact time of 1 hour using 150 ml synthetic grey water solution

The linearised form of the Langmuir and Freundlich isotherm models were fitted to the batch experiment data as shown in Figure 4.23 and Figure 4.24. The linearised isotherm models were fitted to the initial low concentration region of the COD isotherm curve (0 – 180 mg/l), which represents the first monolayer adsorption. A linearised adsorption isotherm model was also fitted to the entire concentration range of the anionic surfactant isotherm data. The aim is to determine which adsorption isotherm model best described the experimental data. The regression correlation coefficient R^2 value was used to determine the goodness of fit.

Table 4.4 - Langmuir and Freundlich isotherm parameters obtained from fitting the isotherm models to experimental data, test was carried over a contact time of 1 hour using 150 ml synthetic grey water solution

	Langmuir				Freundich		
Contaminant	K_L	b	q_m (mg/g)	R^2	K_F	n	R^2
COD	0.11	0.0073	15.3	0.92	0.48	1.8	0.9
Anionic surfactant	0.028	0.085	0.33	0.99	0.04	2.04	0.88

It can be seen from the plot and the R^2 value shown in Table 4.3 that the adsorption of organic grey water contaminants (COD) and anionic surfactants onto Nyex™ adsorbent correlated with the Langmuir adsorption isotherm model for the range of concentrations fitted to the model. The high R^2 of 0.99 observed for the Langmuir fit on the adsorption of anionic surfactant, is evident that adsorption of anionic surfactant molecules onto Nyex™ adsorbent forms only

monolayer adsorption. A maximum monolayer adsorption onto Nyex™ adsorbent was estimated as 15.5 mg/l and 0.33 mg/l for COD and anionic surfactant respectively. The low monolayer adsorption capacity of anionic surfactant onto Nyex™ is due to highly competitive organic molecules present in the SGW as discussed earlier in section 15.2.

4.1.4 Summary

The characteristics of Nyex™ adsorbent in the removal of contaminants from grey water was investigated. Batch experiments were carried out by mixing known concentration of SGW with a selected dose of Nyex™ in a 250 ml Erlenmeyer flasks using an orbital shaker. In order to determine the mechanism of adsorption and the equilibrium characteristics, the experimental results were fitted to well-developed adsorption kinetic and adsorption isotherm models. The effect of initial grey water concentration and adsorbent dosage were also investigated.

Data presented in this part of the thesis demonstrate that Nyex™ adsorbent is only able to remove organic contaminants from grey water. Removal of organic contaminants was investigated based on COD and anionic surfactant values. A 20% reduction in COD value was achieved with an adsorbent loading of 7 g/l at initial COD concentration of 925±100 mg/l.

However, only a 4% reduction was achieved for the removal of anionic surfactant contaminants. The lower percentage removal of anionic surfactant is due to competitive adsorption between anionic surfactant molecules and other organic molecules present in the SGW. Competitive adsorption was investigated by conducting the same experiment using SGW formulated using sodium laureate sulphate (SLS). Removing other organic compounds from the SGW resulted in a 20% increase in the adsorption capacity, thus demonstrating the initial assumption of competitive adsorption between organic contaminants. Results also showed that the initial uptake rate of organic contaminants by Nyex™ is very high at high initial concentration, with the majority of the active adsorption site being occupied within a minute. This is most likely due to the non-porous nature of the Nyex™ adsorbent which eliminates the intra-particle/pore diffusion step of the adsorption process.

The study conducted to investigate the mechanism of adsorption demonstrated that the pH of the SGW solution influenced the adsorption process only at low pH. At solution pH below 4, adsorption is more favourable, an increase in adsorption capacity was observed as the pH is

reduced from 4 to 2. This is due to excess H+ ions present on the surface of the Nyex™ at low pH which is electrostatically attracted to the anionic organic compounds present in the SGW. On the other hand, at a solution pH above 4, there was no significant change in the adsorption of organic contaminants. Data also showed that the presence of electrolyte in the SGW solution had negligible effects on adsorption of organic contaminants.

The pseudo-second order adsorption kinetic model provided the best fit for the adsorption kinetic data with an estimated adsorption capacity and rate constant of 41.7 mg/g and 0.05 g/mg min respectively for grey water with initial COD concentration of 925±100 mg/l. A pseudo-second order fit denotes that adsorption of organics onto the surface of Nyex™ is predominantly by chemical adsorption. It was also observed that the uptake rate and treatment efficiency of organic contaminants by Nyex™ increased with increasing initial grey water concentration. The rapid initial uptake rate is as a result of high concentration difference driving force.

The adsorption isotherm curve illustrates multi-layer adsorption of organic contaminants onto Nyex™, with strong chemical adsorption on the surface of the Nyex™ and then subsequent layers are formed via Van der Waals bond formation. However, adsorption of anionic surfactant is monolayer where the hydrophobic tail adsorbs to the Nyex™ and with a free hydrophilic head. This alignment of surfactant reduces the chances of multilayer formation as the free hydrophilic head has a greater affinity to water molecules in the grey water solution than other surfactant molecules. A linearised adsorption isotherm model was fitted to the monolayer adsorption data for COD and anionic surfactant. The resulting plot showed that the experimental isotherm data for COD and anionic surfactant were better represented by the Langmuir isotherm model. This supports the initial assumption that the adsorption rate is proportional to the concentration driving force and the amount of available adsorption site. The estimated monolayer adsorption capacity for COD and anionic surfactant was 15.5 mg/g and 0.33 mg/g respectively. The low monolayer adsorption capacity for anionic surfactant is due to competitive adsorption between anionic surfactant molecules and other organic molecules.

The effect of Nyex™ dosage was also investigated. Results show that the uptake of organic contaminant and of anionic surfactant is directly proportional to the adsorbent loading, however this proportionality is only limited to below 150 g/l of Nyex™ for COD. It was also observed that the uptake of anionic surfactant is more dependent on the adsorbent dosage. This is due to

the increase in adsorption surface with increase in adsorbent loading, thus resulting in a higher uptake of anionic surfactant. The reduction in the amount of COD removed is due to increased likelihood of the adsorbent coagulating at the basal plane with increasing adsorbent dosage, as well as a reduction in the concentration driving force.

The general conclusion from the batch adsorption study is that adsorption of organic contaminants from SGW can be achieved using Nyex™ adsorbent. The organic contaminants are chemisorbed onto the surface of Nyex™ and a multilayer adsorption was observed only for COD value. Anionic surfactant on the other hand was only able to adsorb on Nyex™ as a mono-layer arrangement.

4.2 Electrochemical Regeneration of Nyex™

4.2.1 Introduction

This section of the thesis presents data obtained from evaluation of the batch electrochemical regeneration process. The adsorbent was initially saturated by allowing the adsorption process to reach equilibrium (1 hour contact time). Electrochemical regeneration of the saturated adsorbent was then conducted at various operating conditions. Repeated regeneration of Nyex™ was also investigated with the operating conditions kept constant for each regeneration trial. In the following section, the influence of various electrochemical regeneration parameters was evaluated along with the influence of repeated regeneration cycles.

Electrochemical regeneration of the saturated adsorbent is required in order to restore its adsorptive capacity. Electrochemical regeneration involves the removal of adsorbed organic contaminant from the surface of the adsorbent by applying electric current across an electrochemical cell packed with the adsorbent. Ideally, electrochemical regeneration should enable complete oxidation of the adsorbed organic compounds (so that they are not transferred from the adsorbed phase to the bulk liquid phase) and thus allow restoration of the full adsorptive capacity of the adsorbent. The performance of the electrochemical process was evaluated by estimating the percentage regeneration efficiency (%RE) which is defined as a ratio between the adsorptive capacity of the regenerated and fresh adsorbent.

In order to achieve electrochemical regeneration, sufficient current is required. Electric current is defined as the rate of flow in electric charge. To obtain a high operating charge, an increase in electron concentration is required. This can be achieved by increasing the current which in turn increases the number of electrons passing through the system within a given time. Another possible method of increasing the charge is by increasing the regeneration time which again enables passage of a high number of electrons across the cell. Hence the charge passed, taking into account the current and treatment time was estimated and its effect on regeneration efficiency was evaluated. The effect of electrolyte concentration and organic loading on regeneration efficiency was also investigated.

4.2.2 Evaluation of electrochemical regeneration parameters

4.2.2.1 Electrolyte concentration

The use of electrolyte in the electrochemical cell increases the electric conductivity and as a result increases the efficiency of the electrochemical regeneration process. Of all the possible electrolytes reported by numerous researchers, sodium chloride (NaCl) has been found to be the most effective in providing high regeneration efficiency (Brown et al. 2004b; Karimi-Jashni and Narbaitz 2005; Taiwo and Adesina 2005; Zhang 2002; Narbaitz and Cen 1994). For this reason, NaCl was used as the supporting electrolyte in this research. The result presented in Figure 4.25 supports the benefits of using NaCl. As the concentration of NaCl increased from 0 to 3% w/v the regeneration efficiency also increased from around 60% to 100% respectively. In addition, increase in the NaCl concentration resulted in a reduction in the operating voltage from 16 V to 7 V, due predominantly to the high electrical conductivity of the electrolyte solution. Reduction in the operating voltage is an advantage as it means significant decrease in the electric energy cost. The effect of NaCl on %RE appears to be more significant at concentration below 2% w/v, above which the increase in percentage %RE was not very significant. However, an electrolyte concentration of 3% w/v was selected to ensure high removal efficiency as well as low operating voltage.

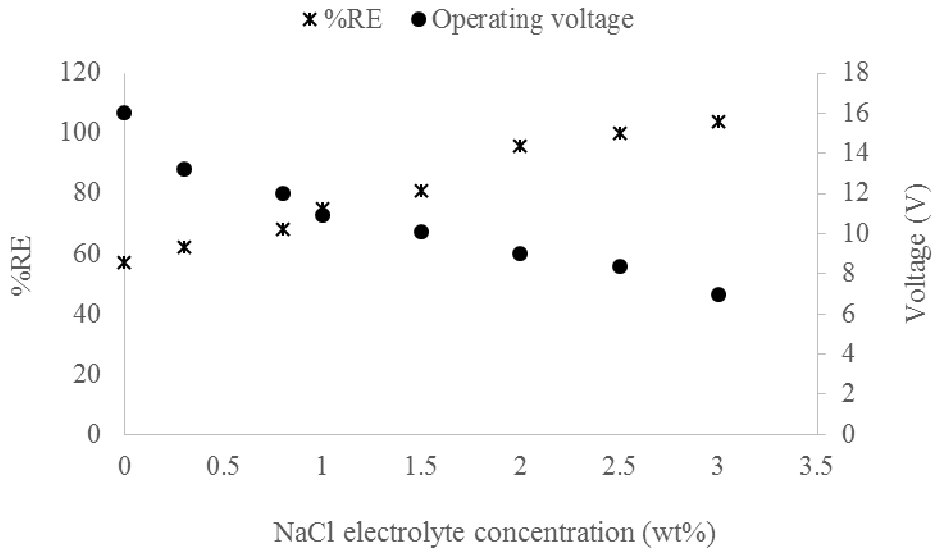


Figure 4.25 - Regeneration efficiency of Nyex™ at different electrolyte concentration using 250 ml SGW with initial COD concentration of 200 ± 20 and with 500 g/l of Nyex™. Charge passed across the cell was 0.5 C/g

4.2.2.2 Charge passed across the electrochemical cell

The plot in figure 4.26 provides a comparison between the percentage RE and charge passed across the cell. The charge passed is presented in terms of charge per mass of Nyex™ used. It was found that the full adsorptive capacity of the adsorbent was recovered after 30 minutes of regeneration with a current density above 30 mA/cm^2, thus corresponding to a charge of 22 C/g. However, at an operating current density of 30 mA/cm^2 the full adsorptive capacity of the adsorbent was not recovered at regeneration time below 30 minutes. The fact that complete regeneration of the adsorbent can be achieved means that the adsorbed organic contaminants has been completely oxidised, forming non-polar by-products which has very low affinity to the adsorbent. If organic compounds were generated as by-products, it would most likely adsorb on the regenerated adsorbent and thus hinder further adsorption. Hence, although further work is required to determine the breakdown products, it is likely from the results obtained that organics are not involved in the breakdown products generated during the electrochemical regeneration process.

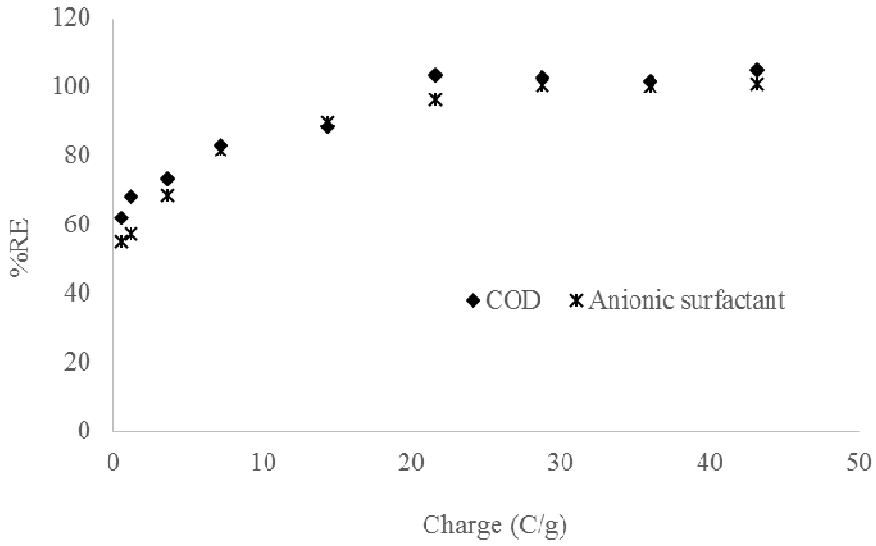


Figure 4.26 - Effect of charge passed on the regeneration efficiency of organic contaminants during electrochemical regeneration of Nyex™; test was conducted using 250 ml grey water solution, with 250 g/l Nyex™ and initial COD and anionic surfactant concentration of 200±20 and 25±6 mg/l respectively

Furthermore, it can be seen from the plot that the %RE increased with an increase in the charge passed, approaching a maximum regeneration efficiency after a charge of 22 C/g is passed.

Increasing the charge above 22 C/g did not result in further increase in regeneration efficiency for both anionic surfactants and COD. Similar COD trend was observed by Brown et al. 2004b and Mohammed (2011) using Nyex™ for the adsorption of crystal violet dye. An optimum charge of 25 C/g was reported by Brown et al. (2004b) and Mohammed (2011) reported an optimum charge of 20 C/g both of which corresponds fairly well with the value obtained in this project.

4.2.2.3 Organic load

The impact of organic loading on the electrochemical regeneration process was assessed by plotting the %RE against the equilibrium solid/adsorbed phase concentration (Figure 4.27). The figure demonstrates an improvement in regeneration efficiency upon increase in the solid phase concentration for both anionic surfactants and COD. This indicates that at a high contaminant load (high solid/adsorbed phase concentration), the majority of charge passed is used for oxidising the contaminants rather than for other side reactions thus increasing the %RE (Wang 2003; Nelson 2002; Jüttner 2000).

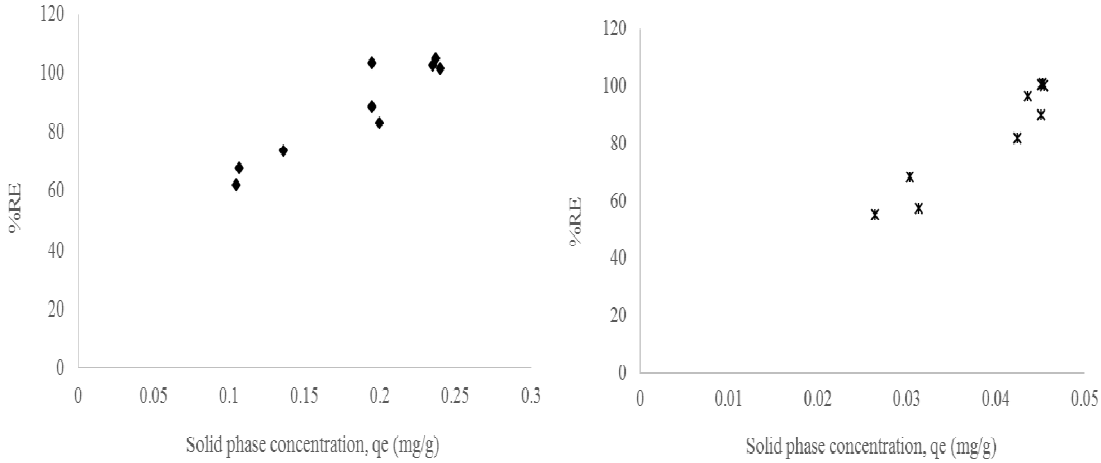


Figure 4.27 - Regeneration efficiency as a function of solid/adsorbed phase concentration at equilibrium.; test was conducted using 250 ml SGW solution, with 250 g/l Nyex™ and initial concentrations of 200±20 and 25±6 for (a)COD and (b) anionic surfactants respectively

4.2.3 Evaluation of regeneration cycle

The electrochemical process was repeated over 7 cycles with the aim of studying its influence on the regeneration efficiency and thus determines if the adsorbent can be recycled over

prolonged use. Tests was conducted using the optimum charge of 22 C/g as well as charges below the optimum charge (3 C/g, 14 C/g), a blank trial was also conducted in which no charge was passed across the cell. Each regeneration cycle was carried out under the same operating conditions.

When a charge of 22 C/g was passed across the cell the regeneration efficiency was maintained at around 100% over the 7 cycles investigated. However when the charge passed was 14 C/g, there was a steady reduction in the regeneration efficiency of around 20% over the 7 cycles (Figure 4.28 and 4.29). In the case of the blank trial where no charge was passed across the cell, the reduction in regeneration was rapid, with an 80% reduction in regeneration efficiency over 4 cycles. Passing a charge of 22 C/g resulted in an adsorption capacity of around 5% greater than the adsorption capacity of fresh Nyex™ as indicated by the slight increase in %RE above 100%. It has been suggested that the increase in the adsorption capacity of the regenerated Nyex™ adsorbent is due to increase in acidic oxygen base functional groups on the surface of the Nyex™ adsorbent (Nkrumah-Amoako et al. 2014).

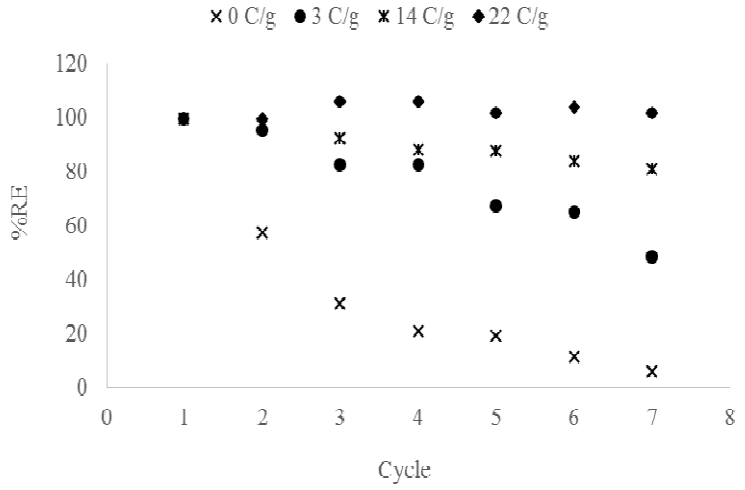


Figure 4.28 - Comparison of the performance of 7 adsorption/regeneration cycles at charges between 0 C/g and 22 C/g; test was conducted using 250 ml of SGW solution with initial COD concentration of 200±20 and with 250 g/l of Nyex™

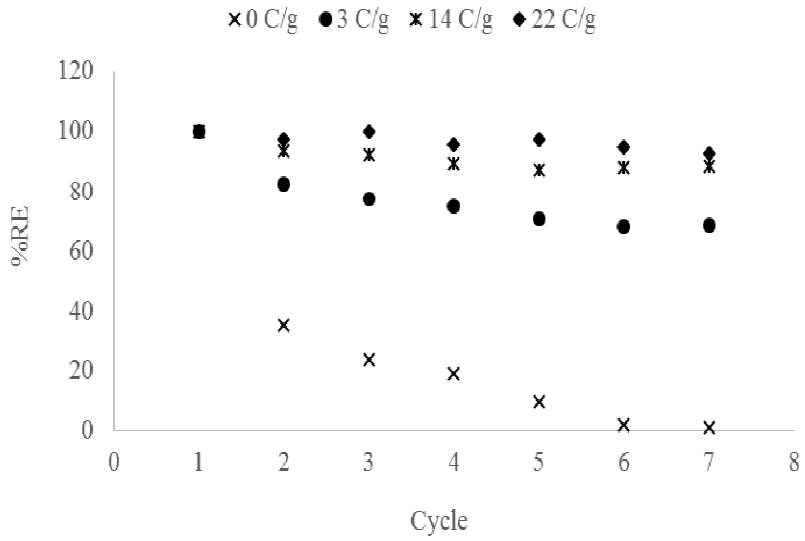


Figure 4.29 - Comparison of the performance of 7 adsorption/regeneration cycles at charges between 0 C/g and 22 C/g; test was conducted using 250 ml of SGW solution with initial anionic surfactant concentration of 25±6 and with 2500 g/l of Nyex™

4.2.4 Summary

Increasing the electrolyte concentration (which in this case was NaCl) from 0 to 3% w/v led to an increase in the regeneration efficiency from 60 to 100% respectively. There was also a reduction in the operating voltage from over 16 V to 7 V as the electrolyte concentration is increased from 0 to 3%. The increase in %RE was less significant above an electrolyte concentration of 2% w/v, although there was a steady decrease in operating voltage above this electrolyte concentration. Based on this data, a 3% w/v was selected as the electrolyte concentration for further experiments.

An investigation on the influence of charge on the electrochemical regeneration demonstrate that the full adsorption capacity of the adsorbent can be achieved using a charge or 22 C/g of Nyex™. Complete regeneration of the adsorbent indicates that no organic by products are generated during the electrochemical regeneration process. This implies complete electrochemical oxidation of adsorbed organic contaminants to a compound with low affinity to the Nyex™ adsorbent.

It was also observed that increasing the adsorbed phase concentration resulted in an increase in the %RE. Data showed that the adsorbent can maintain its adsorptive capacity over several adsorption and electrochemical cycles.

4.3 Breakthrough Study of Electrochemical cell/Packed Bed

The aim of this chapter is to present findings from work undertaken to evaluate the effectiveness of the electrochemical cell in treating grey water. The electrochemical cell was operated in continuous mode, with a packed adsorbent bed made up of 1.2 kg of Nyex™. Details of the experimental procedure as well as a description of the experimental device can be found in section 3.2.2. Breakthrough studies were conducted to evaluate the adsorption profile of the packed adsorbent bed at various operating parameters, and studies were conducted with and without electrochemical regeneration.

This chapter has been divided into two main sections, the first of which presents data obtained from continuous adsorption operation without regeneration (section 4.3.1). In section 4.3.1, the adsorption efficiency of the packed adsorbent bed was evaluated. It is further divided into subsections where the effect of key operating parameters on the breakthrough profile is discussed. The second section (section 4.3.2) presents findings obtained from the continuous adsorption process with electrochemical regeneration, to evaluate the electrochemical regeneration efficiency. Again this section is further divided into subsections discussing the effects of important operating parameters on the breakthrough profile. Studies undertaken to investigate the adsorption and electrochemical regeneration efficiency of an electrolyte free system is also included in the final part of this chapter.

4.3.1 Adsorption without electrochemical regeneration

4.3.1.1 Introduction

The dominant performance indicator for an adsorber is the hydraulic loading rate, adsorbate loading rate and retention time, all of which can be managed by controlling the feed flowrate and the initial adsorbate concentration. Hydraulic loading rate is defined as the flowrate per unit area of packed adsorbent bed. The optimum feed flowrate of the adsorption system depends on the required retention time as well as the hydraulic loading rate. A low feed flowrate increases the retention time which would therefore increase the time at which the adsorbate molecules and the adsorbent are in contact, thus potentially increasing the amount of adsorbate molecules adsorbed. However, previous adsorption kinetics studies have shown that adsorption of organic contaminants onto Nyex™ adsorbent is very rapid, with the majority of adsorption occurring within a minute. This could mean that a high retention time is not required thus

implying that the system may not depend on the feed flowrate. On the other hand, a high feed flowrate not only reduces the retention time, but would also increase the amount of adsorbate molecules in the system at a given time.

Adsorbate loading rate is defined as the mass of adsorbate divided by the area of the packed adsorbent bed, and at a constant packed bed area can be defined by the initial concentration whereby, increasing the initial concentration results in increased organic loading. This parameter may be important since the adsorption process is driven by concentration difference as demonstrated in chapter 4.2. For this reason, the feed flowrate and initial grey water concentration were used as indicator variables to determine the performance of the continuous adsorption process.

The progress of the grey water concentration as it passes through the packed bed of Nyex™ was recorder to generate breakthrough curves, which were used to evaluate the treatment efficiency of the packed bed. Experimental studies were carried out to evaluate the adsorption breakthrough profile within the packed bed at various feed flowrates and initial grey water concentrations.

4.3.1.2 Evaluation of operating parameter

Feed flowrate

To determine the effect of feed flowrate on the breakthrough and adsorption capacity, studies were performed using synthetic grey water (SGW) with initial COD concentration of 724±80 mg/l, feed flow rates of 5 l/h, 10 l/h and 20 l/h were tested. The pseudo second-order adsorption rate (k_2) estimated from the batch adsorption kinetic model was 0.05 g/mg min (section 15.3.6). Based on the Langmuir isotherm curve discussed in section 15.3.7 the adsorption capacity (q_e) at initial feed concentration of 724±50 mg/l was around 20 mg/g (based on the isotherm curve) and the Langmuir constant related to the affinity of binding (K_L) was estimated as 0.11 l/g. With a packed Nyex™ bed of 1.2 kg and initial feed concentration of 724±80 mg/l, the volume of grey water which can be treated was estimated as 33 litres. So at 10 l/h the breakthrough time should be 3.3 hours and 1.65 hours for feed flowrate of 20 l/h.

The breakthrough curves illustrated in Figure 4.30 and Figure 4.31 for COD and anionic surfactant respectively are non-symmetrical breakthrough curves, which imply poor use of the packed bed. A slight increase in the breakthrough concentration was noted as the flowrate was

increased. For instance, the breakthrough concentration for COD at feed flowrate of 20 l/h was 0.65 compared to lower breakthrough concentration of 0.54 observed at feed flowrate of 5 l/h. The plot also reveals that although the breakthrough concentration was around 20% and 34% higher at feed flowrate of 20 l/h compared to 5 l/h for COD and anionic surfactant respectively, the breakthrough of organic contaminants occurred within a minute at all flowrates studied. However, a breakthrough time of over an hour was previously estimated based on the batch equilibrium isotherm characteristics of Nyex™ for COD, which again suggests poor use of the packed adsorbent bed.

Furthermore, in order to achieve the necessary treatment consent of 28 mg/l COD (section 2.2.2), based on an initial COD concentration of 724 mg/l, a breakthrough concentration of less than 0.04 or 4% breakthrough was required. This means that at 54% breakthrough, the system does not meet the treatment requirement for grey water even at a very low flowrate of 5 l/h.

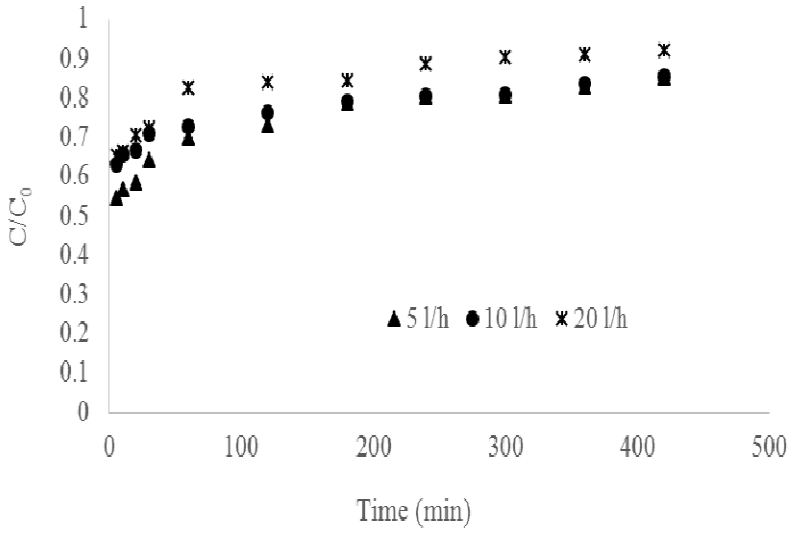


Figure 4.30 - Breakthrough curve: effect of flow rate on the adsorption of organic contaminants from grey water based on COD value; Studies conducted at room temperature, with feed/influent flow rates of 5 l/h, 10 l/h and 20 l/h, influent COD concentration of 724±80 mg/l, pH of the system remained at 6.8±5 and no current was passed across cell

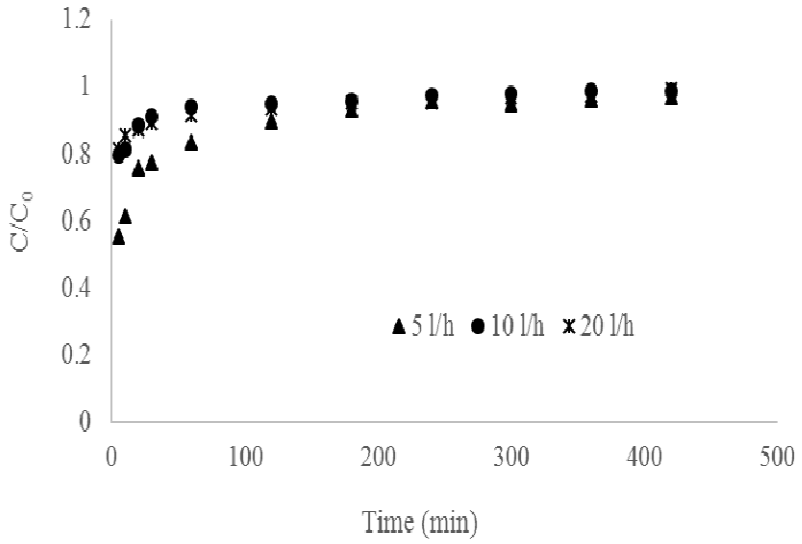


Figure 4.31 - Breakthrough curve: effect of flow rate on the adsorption of anionic surfactants from grey water; Studies conducted at room temperature, with feed/influent flow rates of 5 l/h, 10 l/h and 20 l/h, influent anionic surfactant concentration of 50±10 mg/l, pH of the system remained at 6.8±5 and no current was passed across cell

In addition, the packed bed saturation time seemed to be fairly similar for all flowrates tested for both COD and anionic surfactant. The shape of the breakthrough curves were also comparable for all flowrates studied, and there appear to be no shift towards the time axis with changes in feed flowrate. This suggests that increasing the flowrate from 5 l/h to 20 l/h and thus the residence time, did not have a significant effect on the treatment efficiency. Although, it was expected that operating at a higher feed flowrate should result in a more rapid bed exhaustion time. The non-symmetrical shape of the breakthrough curves and the very short breakthrough time observed was brought about as a result of flow channelling or bed spouting (Holdich 2002). Flow channelling occurs when the fluid flowing through the packed bed finds a preferred path and thus does not distribute evenly through the packed bed. The image depicted in Figure 4.32 was taken from the process and provides evidence of flow channelling through the packed bed. Occurrence of non-symmetrical curves due to flow channelling is induced by high feed flowrate or poor fluid distribution (Holdich 2002), which therefore result in premature breakthrough time. Since the feed flowrate investigated in this study was fairly low, it can be concluded that the presence of flow channelling was mainly due to poor fluid distribution by the nozzle installed on the electrochemical cell.

Figure 4.32 - Flow profile of grey water through the packed bed of Nyex™ adsorbent in the electrochemical cell

Initial feed concentration

Experiments were also carried out to investigate the effect of initial grey water concentrations on the breakthrough profile. Three different concentrations were tested at flowrate of 10 l/h. The resulting breakthrough curve from the test is illustrated in Figure 4.33 and Figure 4.34 for COD and anionic surfactant respectively. It can be observed from Figure 4.33 that increasing the concentration of organic contaminants did not result in a substantial change in the breakthrough concentration. For instance, the breakthrough concentration (C/C_0) was 0.63 for an initial COD concentration of 725 mg/l whilst at an initial COD concentration of 83 mg/l, the breakthrough concentration was 0.62. Increasing the feed concentration did not seem to affect the bed exhaustion time either, which was unexpected as increasing the concentration should result in a shorter bed exhaustion time. The breakthrough curves for anionic surfactants shows a general increase in the breakthrough concentration from 0.338 to 0.79 as the feed concentration is increased from 9 mg/l to 57 mg/l (Figure 16.5). Furthermore, the non-symmetrical shape of the breakthrough curve observed as well as the short breakthrough time provides further indication of flow channelling through the packed bed (Moraes et al. 2000).

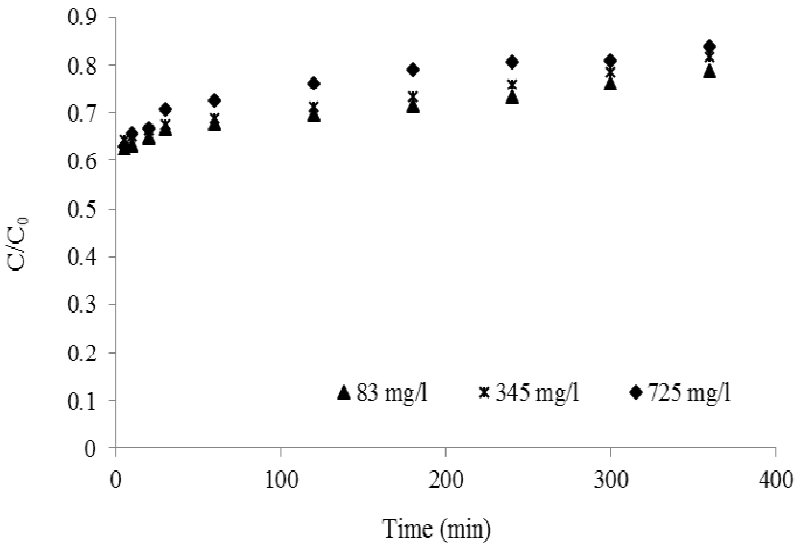


Figure 4.33 - Breakthrough curve: effect of initial influent concentration on the adsorption of organic contaminants from grey water based on COD value; Studies conducted at room temperature, with initial influent COD concentrations of 83±10 mg/l, 345±40 mg/l and 724±80 mg/l, influent flowrate of 10 l/h, pH of the system remained at 6.8±5 and no current was passed across cell

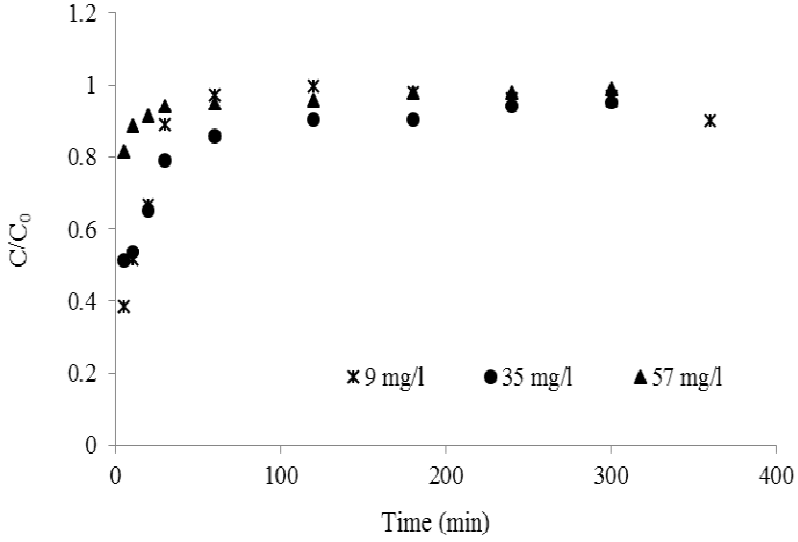


Figure 4.34 - Breakthrough curve: effect of initial influent concentration on the adsorption of anionic surfactants from grey water; Studies conducted at room temperature, with initial influent anionic surfactant concentrations of 9±2 mg/l, 35±5 mg/l and 50±10 mg/l, influent flowrate of 10 l/h, pH of the system remained at 6.8±5 and no current was passed across cell

4.3.2 Adsorption with electrochemical regeneration

4.3.2.1 Introduction

This chapter describes results obtained from grey water treatment by continuous adsorption and electrochemical regeneration at various operating conditions. In order to investigate the effect of passing an electric current across the packed bed of Nyex™ on the treatment efficiency, SGW with an initial concentration of 724±80 mg/l was pumped through the electrochemical cell at a range of flowrates (5, 10, 20 and 30 l/h). For each set of experiments, the electrochemical cell was operated continuously for a minimum of 3 hours and the current density was varied between 0 mA/cm^2 to 16 mA/cm^2 which corresponds to a charge of 0 C/g to 90 C/g over the treatment time.

The main operating parameters investigated were feed flowrate and the electric charge passed across the system. The performance of the system was defined using the breakthrough curve profile, the treatment efficiency and the current efficiency.

Test results presented in the previous section of this chapter demonstrated poor breakthrough performance due to inefficient use of the full adsorption capacity of the bed as a result of flow channelling. Results obtained during the batch electrochemical regeneration tests discussed earlier in section 4.2, showed that the Nyex™ adsorbent can be regenerated to full adsorption capacity with a minimum charge of 22 C/g. It was therefore expected that passing sufficient electric charge across the cell should increase the treatment efficiency of the system, by destroying adsorbed organic contaminant molecules thus providing active adsorption sites for molecules in the bulk liquid phase.

4.3.2.2 Evaluation of operating parameters

Current density

The current density is a measure of the electric current and takes into account the area of the electrode used in the electrochemical cell. It plays a major role in the design of the adsorption and electrochemical regeneration system. The breakthrough curves depicted in Figure 16.6 was obtained for a number of current densities (0, 3.2, 8, 12.8, 14.4 and 16 mA/cm2) by maintaining the operating flowrate at 10 l/h and with an initial SGW concentration of 724±80 mg/l. It can be seen from the plot (Figure 4.35 and Figure 4.36) that the breakthrough time was very short for both COD and anionic surfactant, with breakthrough occurring immediately. The short

breakthrough time as well as the non-symmetrical shape of the breakthrough curve was similar to the curve obtained for adsorption studies without electrochemical regeneration, thus suggesting that passing an electric current across the bed had no effect on the breakthrough time. This result provide further evidence that flow channelling was occurring within the packed bed, whereby the influent grey water solution was not distributed evenly and was therefore bypassing the bed.

A reduction in the breakthrough concentration ratio (C/C_0) was noted for COD and anionic surfactant value when an electric current was applied across the cell. For instance, the breakthrough concentration ratio for COD decreased from 0.62 to 0.36, which is from 62% to 35% breakthrough when a current density of 16 mA/cm^2 was applied. It was also observed that decreasing the current density resulted in an increase in the breakthrough concentration, such that halving the current density from 16 mA/cm^2 to 8 mA/cm^2 led to a 58% increase in the breakthrough concentration. Similarly, there was an increase in breakthrough concentration for anionic surfactant as the current density decreased, although not as much compared to that of COD value. In the case of anionic surfactant, passing a current density of 16 mA/cm^2 decreased the breakthrough concentration from 92% to 62%. Halving the current density from 16 mA/cm^2 led to a 38% increase in the breakthrough concentration.

In addition, the plot illustrates that the system ability to remove organic contaminants from the grey water decreased over time as indicated by the increase in breakthrough concentration over time. This indicates that, the packed adsorbent bed was not able to fully regenerate when the system was operated in continuous adsorption and regeneration mode.

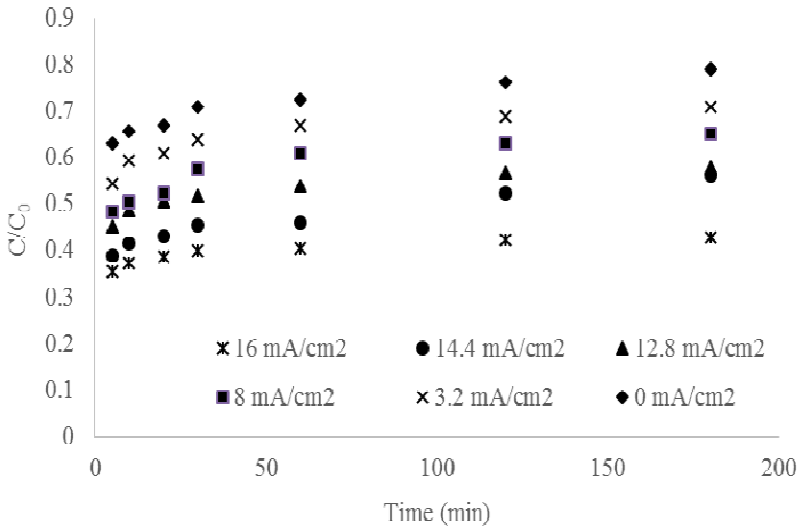


Figure 4.35 - Breakthrough curve: effect of electric current on the removal of organic contaminants from grey water based on COD value, using continuous adsorption and electrochemical regeneration method. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent COD concentration of 724±80 mg/l, influent flowrate of 10 l/h and the pH of the system was around 2±1

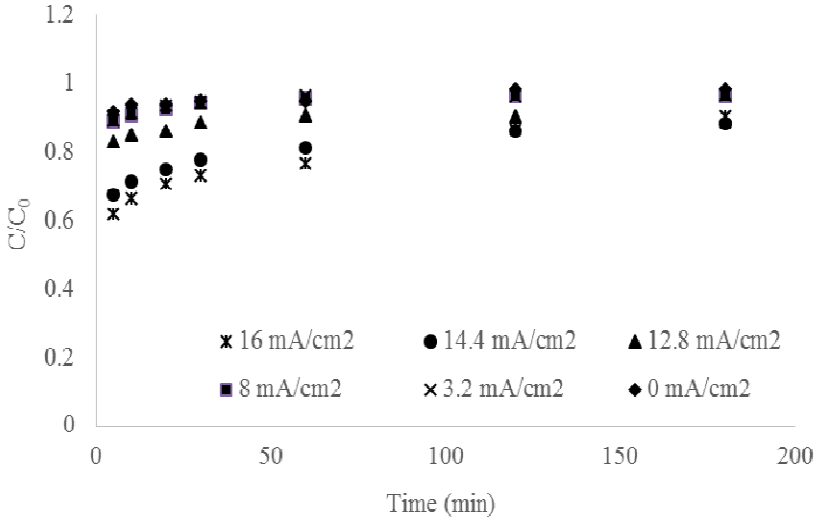


Figure 4.36 - Breakthrough curve: effect of electric current on the removal of anionic surfactants from grey water, using continuous adsorption and electrochemical regeneration method. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent anionic surfactant concentration of 50±10 mg/l, influent flowrate of 10 l/h and the pH of the system was around 2±1

It can be seen from the plot in Figure 4.37 and Figure 4.38 that increasing the current density applied across the electrochemical cell increased the adsorption capacity of the packed adsorbent bed for COD and anionic surfactants. After a treatment time of 3 hours there was a 56% and 87% increase in the adsorption capacity for COD and anionic surfactants respectively when a current density of 16 mA/cm^2 was applied.

In order to further investigate the effect of electrochemical regeneration on the treatment efficiency of the system, the charge passed per mass of Nyex™ adsorbent was investigated. The effect of treatment efficiency on charge passed is presented in Figure 4.39. As expected, the treatment efficiency increased for both COD and anionic surfactants as the charge passed across the system was increased. The plot shows that a treatment efficiency of up to 63% and 25% can be achieved for COD and anionic surfactant respectively at a charge of 90 C/g (equivalent to 16 mA/cm^2). However, increasing the charge resulted in an increase in the cell potential which means a higher operating cost (Figure 4.40).

The effect of charge passed on the current efficiency for COD is illustrated in Figure 4.41. The plot depicts a current efficiency of above 100%, this is due to the fact that electrochemical oxidation was not the only method through which organic contaminants are removed. The effect of adsorption of organic contaminants also taking place in the system led to the high regeneration efficiency observed. Brown (2005) also reported a current efficiency above 100% for the regeneration of Nyex™ saturated with an organic compound, where a current efficiency of 350% was observed with a charge of 5 C/g.

A 30% reduction in current efficiency was observed as the charge passed across the cell was increased from 45 C/g to 90 C/g. The reduction in current efficiency may be attributed to an increase in the amount of charge passed being used for side electrochemical reaction rather than for the destruction of organic contaminants (Brown 2005). This suggests that although operating the system at a high charge enabled higher treatment efficiency, the system might become inefficient and expensive to run due to high power cost. However, to achieve a removal efficiency of above 64% which in this case is necessary in order to meet the treatment consent for grey water, a current density of above 16 mA/cm^2 is required. Although this would be at the expense of a high cell potential and thus high energy cost.

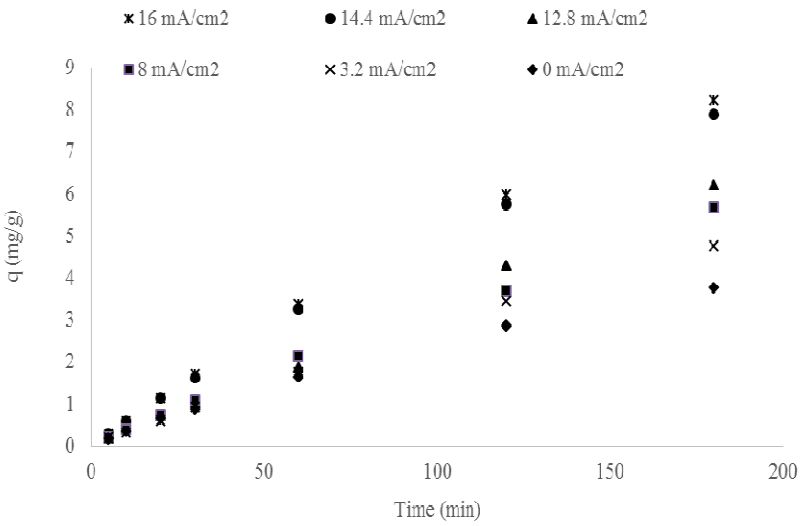


Figure 4.37 - Effect of electric current on the adsorption capacity or adsorbed phase concentration of the packed adsorbent bed over time for organic contaminants. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent COD concentration of 724±80 mg/l, influent flowrate of 10 l/h and the pH of the system was around 2±1

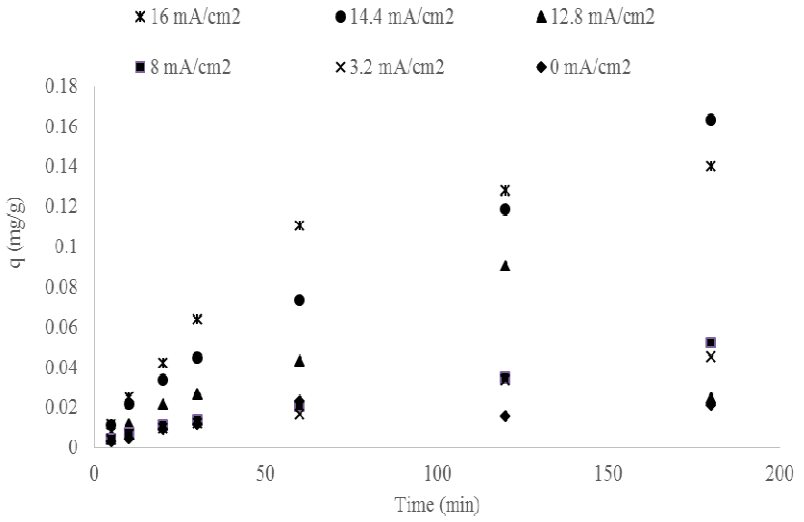


Figure 4.38 - Effect of electric current on the adsorption capacity or adsorbed phase concentration of the packed adsorbent bed over time for anionic surfactants. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent anionic surfactant concentration of 50±10 mg/l, influent flowrate of 10 l/h and the pH of the system was around 2±1

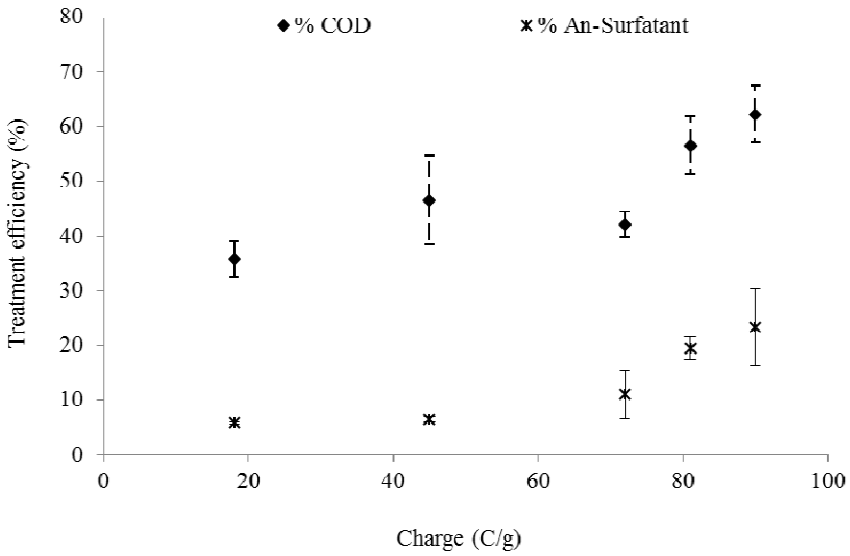


Figure 4.39 - Treatability plot: effect of electric current in terms of charge passed across electrochemical cell on the treatment efficiency of COD and anionic surfactants. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent COD and anionic surfactant concentrations of 724±80 and 50±10 mg/l respectively, influent grey water flowrate of 10 l/h and the pH of the system was around 2±1

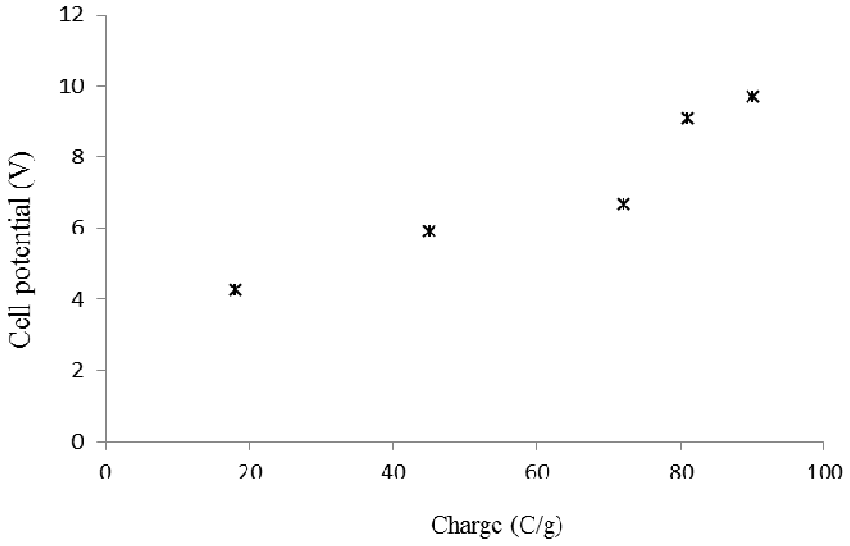


Figure 4.40 - Effect of electric current in terms of charge passed across electrochemical cell on the cell potential. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent COD and anionic surfactant concentrations of 724±80 and 50±10 mg/l respectively, influent grey water flowrate of 10 l/h and the pH of the system was around 2±1

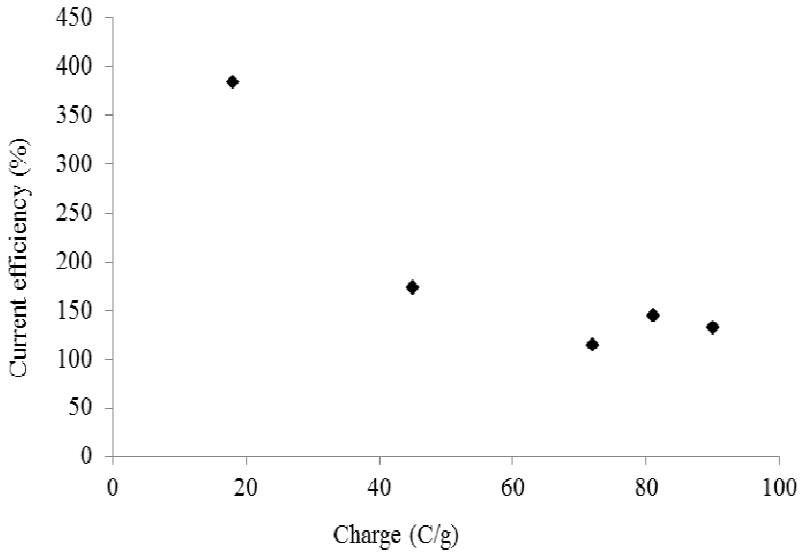


Figure 4.41 - Treatability plot: effect of electric current in terms of charge passed across electrochemical cell on the current efficiency for COD. Studies conducted at room temperature, with current densities of 3.2, 8, 12.8, 14.4 and 16 mA/cm^2 passed across electrochemical cell, influent COD concentration of 724±80, influent grey water flowrate of 10 l/h and the pH of the system was around 2±1

Feed flowrate

The effect of feed flowrate on the treatment efficiency of the adsorption and electrochemical regeneration process was investigated by varying the feed flowrate (10, 15, 20, 30 l/h) with constant current density of 14.4 mA/cm^2. The breakthrough curves obtained for this study are shown in Figure 4.42 and Figure 4.43 for COD and anionic surfactant respectively. As the feed flowrate increased from 10 l/h to 30 l/h, the breakthrough concentration increased from 38% to 47% corresponding to a 20% reduction in the treatment efficiency. A reduction in treatment efficiency of around 22% was also observed for anionic surfactant as the flowrate was increased from 10 l/h to 30 l/h. In addition, increasing the feed flowrate resulted in a slight decrease in the treatment efficiency (Figure 4.44) and the current efficiency (Figure 4.45) for COD and anionic surfactant. It was also observed that the current efficiency for COD was a lot higher than for anionic surfactants. This could be due to the fact that the adsorbed phase concentration for COD was higher for COD than for anionic surfactant, a high adsorbed phase concentration has previously been found to increase regeneration efficiency (section 4.2).

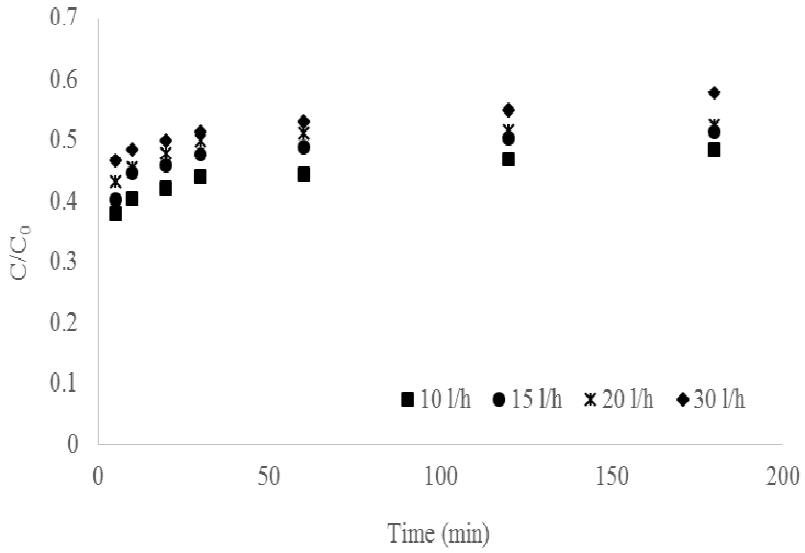


Figure 4.42 - Breakthrough curve: effect of feed concentration on the removal of organic contaminants from grey water based on COD value, using continuous adsorption and electrochemical regeneration method. Studies conducted at room temperature, with feed flow rates of 10 l/h, 15 l/h, 20 l/h and 30 l/h, influent COD concentration of 724±80 mg/l, with current density of 14.4 mA/cm^2 passed across electrochemical cell and the pH of the system was around 2±1

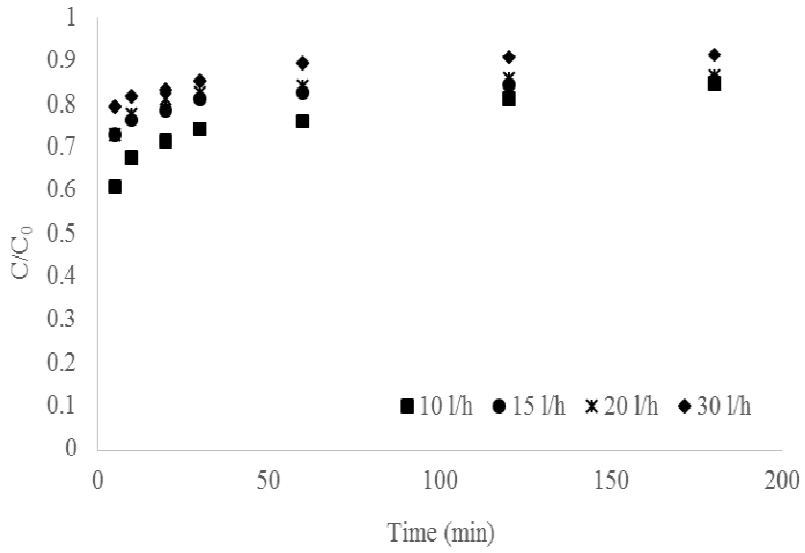


Figure 4.43 - Breakthrough curve: effect of feed concentration on the removal of anionic surfactants from grey water, using continuous adsorption and electrochemical regeneration method. Studies conducted at room temperature, with feed flow rates of 10 l/h, 15 l/h, 20 l/h and 30 l/h, influent anionic surfactant concentration of 50±10 mg/l, with current density of 14.4 mA/cm^2 passed across electrochemical cell and the pH of the system was around 2±1

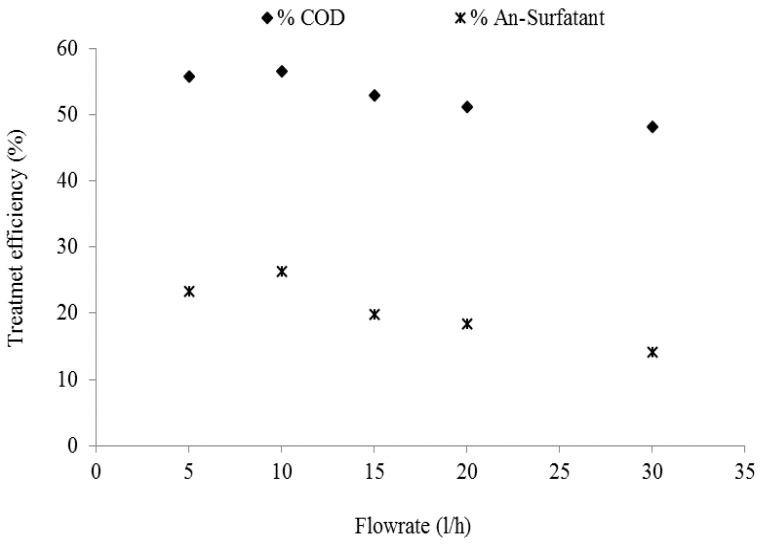


Figure 4.44 - Treatability plot: effect of feed flowrate on the treatment efficiency of COD and anionic surfactants. Studies conducted at room temperature, with feed flowrates of 10 l/h, 15 l/h, 20 l/h and 30 l/h, current densities of 14.4 mA/cm^2 passed across electrochemical cell, influent COD and anionic surfactant concentrations of 724±80 and 50±10 mg/l respectively and the pH of the system was around 2±1

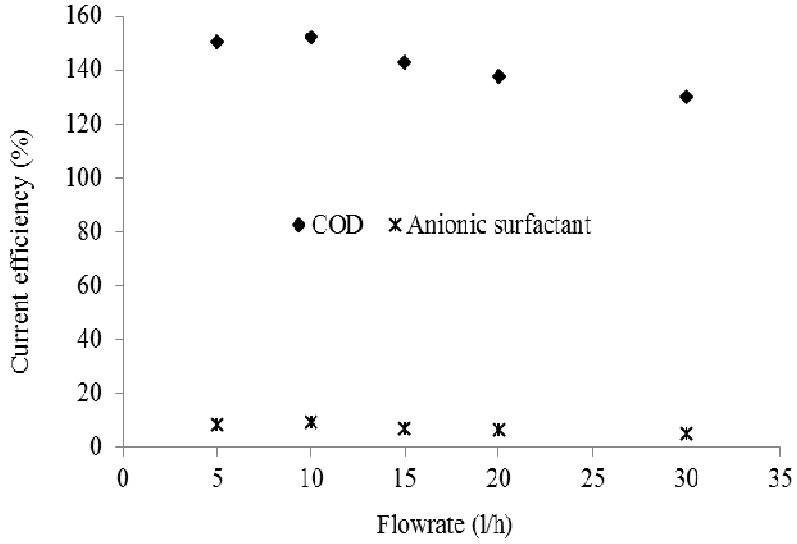


Figure 4.45 - Treatability plot: effect of feed flowrate on the current efficiency for COD. Studies conducted at room temperature, with feed flowrates of 10 l/h, 15 l/h, 20 l/h and 30 l/h, current densities of 14.4 mA/cm^2 passed across electrochemical cell, influent COD concentration of 724±80 and the pH of the system was around 2±1

An increase in the adsorbed phase concentration means that a higher percentage of current passed across the cell is consumed mainly for regenerating the Nyex™ rather than for other side reactions.

Concentration of sodium chloride (NaCl)

During normal operation of the cell, 3% w/v NaCl was added to the system, none of which was removed by the process and thus ends up in the treated grey water. The results in figure 4.46 was obtained from tests carried out to determine the effect of not using NaCl on the performance of the electrochemical regeneration process. It can be observed that although the percentage COD reduction in the continuous adsorption and electrochemical regeneration process was 31% better when NaCl was present, it can be seen that the current efficiency was higher when no NaCl was used (Figure 4.47. However, the cell potential doubles when no NaCl was used. This implies that the presence of NaCl meant more current is used up for side reactions involving oxidation of chloride ions as that could have been the preferred reaction compared to the oxidation of organic contaminant.

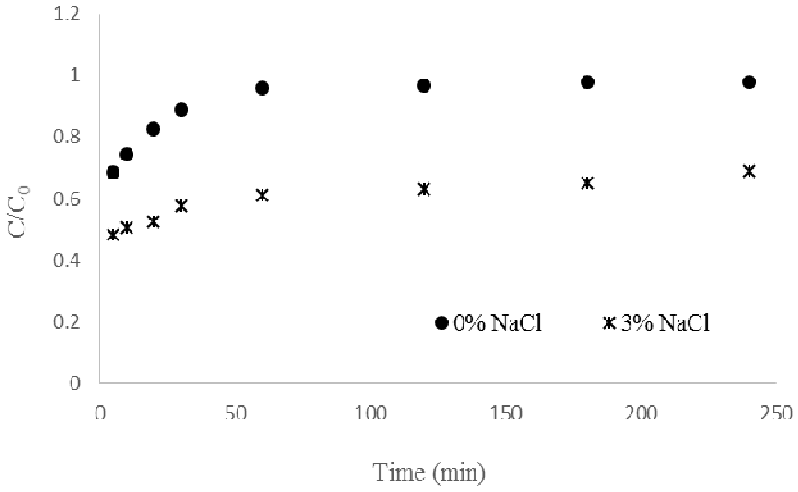


Figure 4.46 - Breakthrough curve: evaluation of a NaCl free system on the removal of organic contaminants from grey water based on COD value, using continuous adsorption and electrochemical regeneration method. Studies conducted at room temperature, with feed flow rates of 10 l/h, influent COD concentration of 724±80 mg/l, with current density of 14.4 mA/cm^2 passed across electrochemical cell and the pH of the system was around 2±1

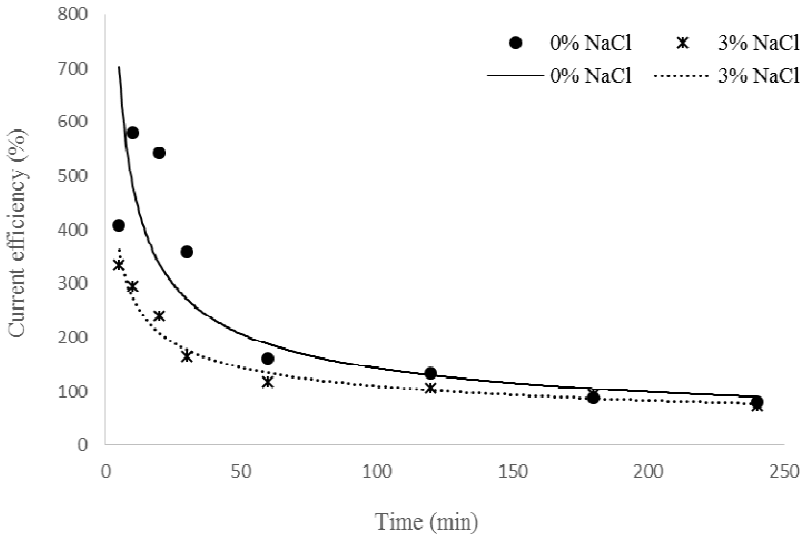


Figure 4.47 - Treatability plot: effect of NaCl electrolyte on the current efficiency for COD. Studies conducted at room temperature, with feed flow rates of 10 l/h, influent COD concentration of 724±80 mg/l, with current density of 14.4 mA/cm^2 passed across electrochemical cell and the pH of the system was around 2±1

4.3.3 Summary

The effectiveness of the electrochemical cell in treating grey water was evaluated in this chapter. The system was operated in continuous mode without electrochemical regeneration to investigate adsorption of organic contaminants by Nyex™ in the electrochemical cell, and with electrochemical regeneration to investigate the regeneration efficiency of the system.

Continuous adsorption without electrochemical regeneration

Results obtained from this study demonstrated poor use of the packed adsorbent bed with breakthrough of organic contaminants occurring immediately. A slight increase in the breakthrough concentration for COD and anionic surfactants was also observed with an increase in the feed flowrate and initial grey water concentration. Furthermore, it was concluded that the non-symmetrical shape of the breakthrough curve, as well as the very short breakthrough time observed for the different feed flowrates and initial grey water concentrations studied was attributed to the presence of flow channelling or bed spouting. The flow channelling resulted in poor distribution of grey water which meant that the full adsorption capacity of the packed bed of Nyex™ was not utilised effectively. This was the main reason why the system was not able to achieve the expected breakthrough time of over 1 hour.

Continuous adsorption with electrochemical regeneration

The results confirmed that electrochemical regeneration of the packed bed of Nyex™ was being achieved. In the absence of electrochemical regeneration, whereby no electric current was applied across the cell, the breakthrough concentration was found to be 0.62 which corresponds to a treatment efficiency of 37%. In contrast, when electric current was applied across the cell, at a current density of 16 mA/cm^2, a treatment efficiency of 63% and 25% was observed for COD and anionic surfactant respectively. Operating the system at a higher current density resulted in an increase in the cell potential as well as a reduction in the current efficiency. An evaluation of the effect of feed flowrate showed that increasing the feed flowrate from 10 l/h to 30 l/h led to a 20% and 22% reduction in the treatment efficiency of grey water for COD and anionic surfactant respectively. Furthermore, it was found that operating the electrochemical cell without NaCl resulted in a 31% reduction in treatment efficiency. A higher current efficiency was also observed, although the cell potential doubled when no NaCl was present due to the low electrical conductivity of the NaCl free system.

4.4 Electrochemical Cell Modelling and Implementation

4.4.1 Introduction

Results from the adsorption and electrochemical regeneration study based on COD values were used as input parameters to model the adsorption of contaminants from grey water under various different operating conditions.

The sections in this chapter include a discussion of the different models used to describe the experimental data with the aim of determining predominant information for design. Three well established mathematical models (adsorption dynamic, scale up and mass balance) were utilised to enable prediction of the breakthrough curve over a number of operating condition. The chapter is divided into two main sections, in the first section, mathematical models were fitted to the experimental data to determine if they were suitable for describing the adsorption process taking place in the electrochemical cell. In the second section, the models which best described the experimental data were subsequently used to predict the breakthrough curve. Adsorption dynamic models using three well known models, Thomas, Adam-Bohart and Yoon-Nelson were initially fitted to the experimental data by linear and non-linear regression in order to determine the characteristic parameters for design. The second model discussed in section 4.4.2 used a scale up approach to describe the conditions of the packed adsorbent bed with the aim of predicting the operation of the system. The system was also modelled as a continuous stirred tank reactor using a mass balance model, results obtained from the model was compared to the experimental data in order to determine useful operating parameters for design.

4.4.2 Modelling of the adsorption profile

4.4.2.1 Evaluation of adsorption dynamic model

Adam-Bohart model

Adam-Bohart model was established based on the assumption that the adsorption rate is proportional to both the concentration of the adsorbate present in the bulk liquid phase and the residual adsorptive capacity of the adsorbent. The linear and non-linear forms of the model are discussed in section 2.4.3 of this thesis. The model involves several important adsorption parameters such as the initial feed concentration (C), saturation concentration/removal capacity (N_0), the superficial velocity (U_0) and the bed height (z). Adam-Bohart model was applied to the experimental data and the constants N_0 and K_{AB} were determined for different operating variables studied.

In order to determine values describing the operational characteristic of the system, a linear form of the Adam-Bohart model was initially fitted to the experimental data (APPENDIX D). This enabled calculation of the bed saturation concentration (N_0) and the kinetic constant (K_{AB}) from the intercept and slope of the linear plot respectively. Respective values of parameters N_0 and K_{AB} for all breakthrough curves evaluated are summarised in Table 4.5.

Table 4.5 - Estimated Adam-Bohart model parameters for adsorption of organic contaminants from grey water onto Nyex™

Adam - Bohart						
Q_f (l/h)	C_0 (mg/l)	charge (C/g)	z_b (cm)	K_{AB} (l/mg h) × 10^{-6}	N_o (mg/l)	R^2
10 l/h	724±50	90	25	1.2	2614	0.76
10 l/h	724±50	81	25	2.6	1091	0.93
10 l/h	724±50	72	25	0.16	145	0.78
20 l/h	724±50	81	25	1.2	2053	0.61
30 l/h	724±50	81	25	1.52	1524	0.89

It can be observed from the table that the saturation concentration of the packed adsorbent bed increased with an increase in the charge passed. The saturation concentration also appeared to be higher as the flowrate was decreased from 30 l/h to 10 l/h. A non-linear plot of the model in comparison to the experimental data is presented in Figure 4.48. The plot shows that the breakthrough concentration (C/C_0) of the curve obtained from the model was above 1, which

cannot be correct as the maximum effluent concentration at bed exhaustion cannot be higher than the feed concentration hence the breakthrough concentration should be below or equal to 1. This indicates poor correlation of the model with the experimental data which reflects less applicability of the model.

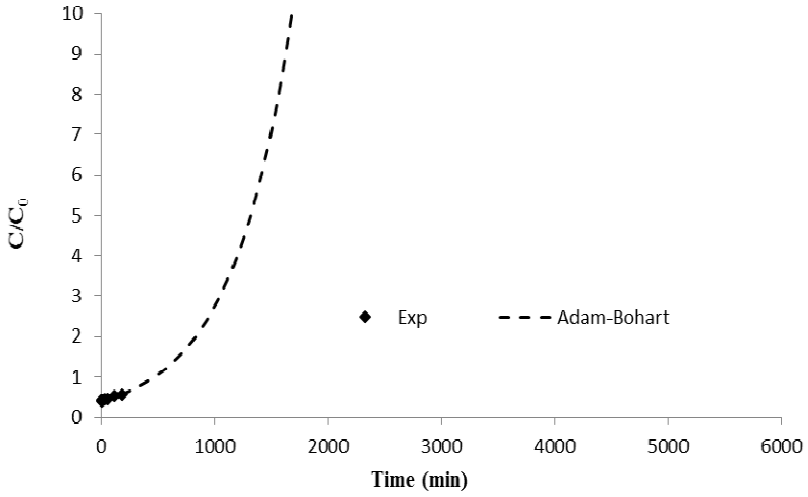


Figure 4.48 - Breakthrough curve: comparison of experimental data with the Adam-Bohart adsorption dynamic model. Experimental data obtained from studies conducted with initial influent COD concentration of 724±80 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm^2

Thomas model

The main assumptions of the Thomas model are that the intra-particle diffusion during the mass transfer process is negligible. The model also assumes that the adsorption process can be described by a pseudo second-order reaction rate principle, which should then reduce to a Langmuir isotherm at equilibrium.

Similar to the Adam-Bohart model, the Thomas model also includes important parameters such as the adsorption capacity of the packed adsorbent bed (q_e), the feed flowrate (Q_f) and the mass of adsorbent (m) all of which can be used in determining the characteristics of the adsorption system. The linear form of the model was fitted to the experimental data to generate a linear plot (APPENDIX D). The rate constant (K_{Th}) and maximum capacity at equilibrium (q_e) of the adsorption process were estimated from the slope and intercept of the linear plot respectively. The determined correlation coefficient and relative estimated constants were obtained and the results are listed in Table 4.6.

It can be seen that the correlation coefficient, R^2, achieved for the majority of the experimental variables was over 0.8. Furthermore, as the feed flowrate increased the value of maximum bed adsorption capacity decreased. A reduction in the maximum bed adsorption capacity from 35 mg/g to 2.5 mg/g was also observed as the charged passed across the cell was decreased from 90 C/g to 72 C/g.

Table 4.6 - Estimated Thomas model parameters for adsorption of organic contaminants from grey water onto Nyex™

Thomas						
Q_f (l/h)	C_0 (mg/l)	charge (C/g)	m (g)	K_{Th} (l/mg h) × 10^{-4}	q_e (mg/g)	R^2
10 l/h	724±50	90	1200	1.2	35	0.98
10 l/h	724±50	81	1200	3	10.4	0.95
10 l/h	724±50	72	1200	2	2.5	0.81
20 l/h	724±50	81	1200	1.4	8.9	0.63
30 l/h	724±50	81	1200	1.8	2.8	0.91

The nonlinear form of the Thomas model was also fitted to the experimental data as shown in Figure 4.49. The plot shows a reasonably good fit of the model to the experimental data, with the system shown to approach equilibrium after a treatment time of around 1020 minutes (17 hours). The Thomas model seem to fit the experimental data fairly well, and thus could be used to predict the breakthrough curve at various operating conditions.

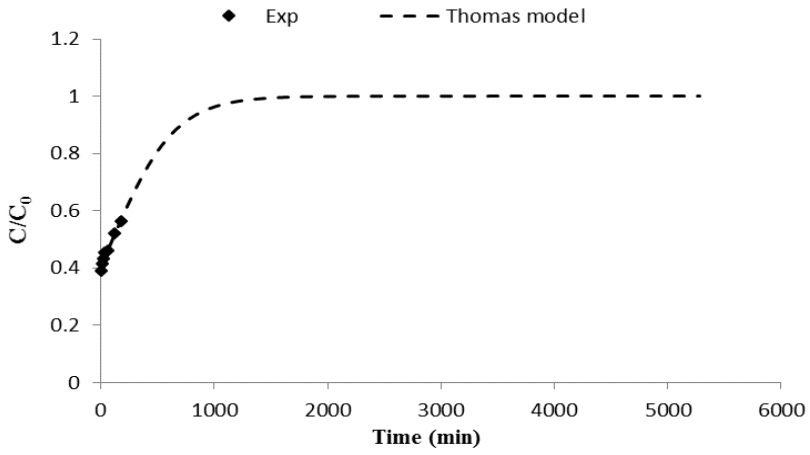


Figure 4.49 - Breakthrough curve: comparison of experimental data with the Thomas adsorption dynamic model. Experimental data obtained from studies conducted with initial influent COD concentration of 724±80 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm²

Yoon-Nelson model

The Yoon-Nelson model takes a very simple and concise form of the adsorption dynamic model. It is based on the assumption that the rate of decrease in the probability of each adsorbate to be adsorbed, is proportional to the probability of its adsorption on the adsorbent.

The linear form of the model was fitted to the experimental data at a range of feed flowrate (10, 20, 30 l/h) and charge (90, 81, 72 C/g). From the slope and intercept of the linear plot (APPENDIX D), the constants of the model, Yoon-Nelson rate constant (K_{YN}) and the time for 50% breakthrough (τ), were determined. Values of the rate constant and 50% breakthrough time along with other parameters are listed in Table 4.7. The time required to achieve 50% breakthrough was found to decrease with a reduction in the charge applied across the cell. In addition, a reduction in the 50% breakthrough time was also observed with an increase in feed flowrate.

Table 4.7 - Estimated Yoon-Nelson model parameters for adsorption of organic contaminants from grey water onto Nyex™

Yoon - Nelson					
Q_f (l/h)	C_0 (mg/l)	charge (C/g)	K_{YN} (h^{-1}) × 10^{-3}	τ (h)	R^2
10 l/h	724±50	90	1.5	340	0.77
10 l/h	724±50	81	3.7	101	0.95
10 l/h	724±50	72	2.4	25	0.81
20 l/h	724±50	81	1.7	88	0.63
30 l/h	724±50	81	2.2	29	0.91

A nonlinear form of the model was fitted to the experimental data and the model fitted fairly well (Figure 4.50), similar to that obtained with the Thomas model. The good fit of the model to the experimental data means the data can be used to predict the breakthrough curve. However, unlike the Adam-Bohart and Thomas models, the Yoon-Nelson model does not include characteristic parameters to enable prediction of breakthrough curves at different operating conditions.

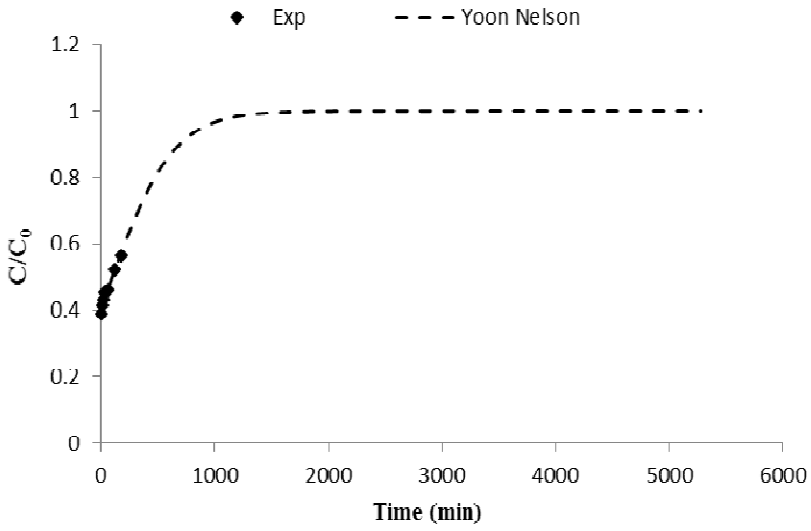


Figure 4.50 - Breakthrough curve: comparison of experimental data with the Yoon-Nelson adsorption dynamic model. Experimental data obtained from studies conducted with initial influent COD concentration of 724±80 mg/l, feed flowrate of 10 l/h and current density of 14.4mA/cm^2

4.4.2.2 Evaluation of scale-up model

The scale up model is based on characteristic parameters describing the breakthrough curve. Characteristic parameters which can be estimated using this model are the mass transfer zone (MTZ) or adsorption zone height (h_z); the MTZ travelling velocity (v_z) and the time required for the MTZ to travel a distance equal to its own length (t_z). The model assumes constant flowrate and initial concentration, negligible accumulation of adsorbate in the void fraction of the bed, isothermal adsorption and formation of a constant pattern of the MTZ (Worch 2012).

The breakthrough time (t_b) was calculated by means of interpolation in the experimental breakthrough data. The breakthrough volume (V_b) was determined at a breakthrough time (t_b) of 0.14 minutes which was the point at which the breakthrough concentration (C/C_0) was 0.01, that is a breakthrough concentration of 1%. A breakthrough concentration of 1% was selected as it is below the allowable treatment consent for COD.

$$V_b = 0.14\,\text{min} \times 10\,\frac{l}{z_b} \times \frac{z_b}{60\,\text{min}} = 0.023\,\text{l} \qquad [4\text{-}1]$$

The bed saturation point was estimated at breakthrough concentration (C/C_0) of 0.95. The bed saturation or exhaustion time was also obtained from the experimental data using interpolation technique, and was estimates as 900 minutes (15 hours). The packed bed saturation volume at a feed flowrate of 10 l/h (V_{sat}) was then estimated as follows:

$$V_{sat} = 15 z_b \times 10\,\frac{l}{z_b} = 150\,\text{l} \qquad [4\text{-}2]$$

The mass transfer zone time was subsequently calculated as:

$$t_z = t_s - t_b = 900 - 0.14 = 899.86\ \text{min} \qquad [4\text{-}3]$$

The symmetry factor (F_S) was calculated from the area of the breakthrough curve as 0.17, the stoichiometric time (t_{st}) was then calculated using Eq. 4-4:

$$t_{st} = t_b + F_S t_z = 0.14 + (0.17 \times 899.86) = 153\ \text{min} \qquad [4\text{-}4]$$

This was then used to estimate the MTZ height using the height of the adsorbent bed (z_b).

$$h_z = z_b \frac{t_z}{t_{st}} = 0.25 * \frac{899.86}{153} = 1.47\ \text{m} \qquad [4\text{-}5]$$

It was noted that at a height of 1.47 m, the height of the mass transfer zone (h_z) was much higher than the actual height of the packed bed (z_b) used to conduct the experiment, which was 0.25 m. This is because the shape of the breakthrough curve obtained from the experiment was not symmetrical, which means the estimated stoichiometric time determined by iterative process is most likely incorrect (Worch, 2012). Therefore the scale-up method was deemed unsuitable for modelling the experimental data.

4.4.2.3 Evaluation of mass balance model

The packed bed system was modelled by assuming that the liquid jet generated from pumping the influent grey water through holes on the nozzle created a series of spouts/channels in the bed, and that an adsorption zone is formulated within the spout (Figure 4.51).

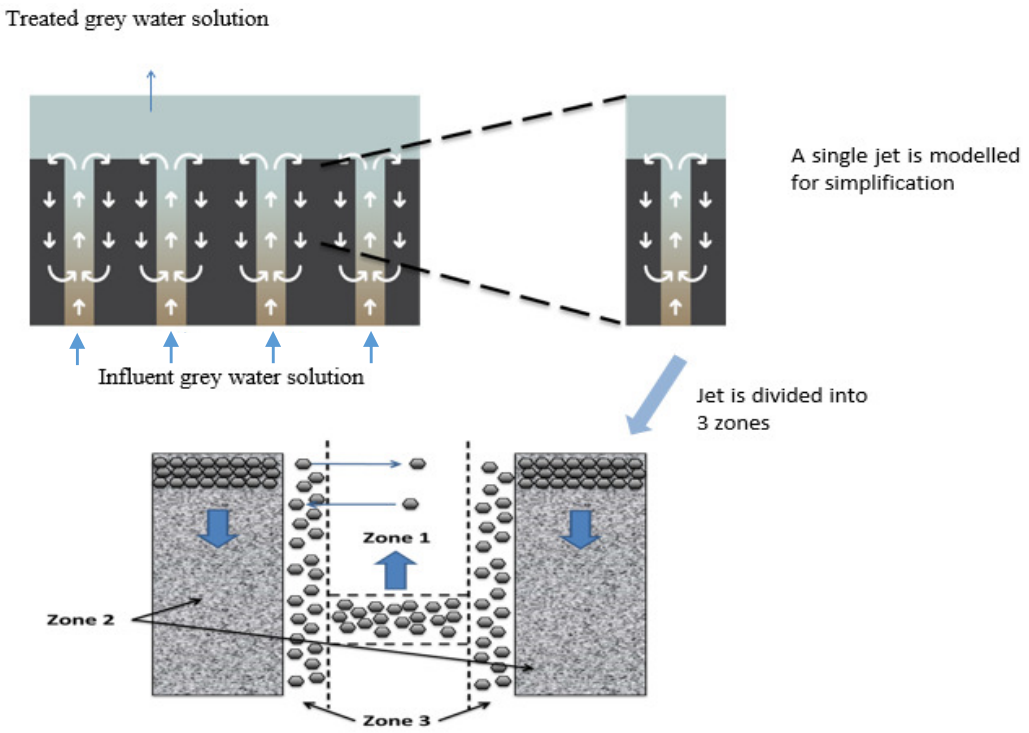


Figure 4.51 - Schematic diagram presenting the different zones in the electrochemical cell

Zone 1 is the fluidised bed zone which is the path by which the liquid jet passes through, and is assumed to be the MTZ or adsorption zone. Grey water solution moves at a constant flowrate

(Q_f, l/min) up the jet and Nyex™ adsorbent moves at a constant flowrate (M_f, g/min) up the liquid jet. It was also assumed that the Nyex™ concentration (m_c, g/l) remained the same.

Zone 2 is the regeneration zone and it was assumed that the amount of adsorption that takes place in this zone is negligible. It was also assumed that the grey water solution and Nyex™ adsorbent both flow as plug flow with the adsorbent moving down the bed, and that the concentration of Nyex™ adsorbent remained the same.

Zone 3 is the intermediate zone where Nyex™ adsorbent migrates back and forth from the packed bed into the liquid jet. It was assumed that there is no net transfer of Nyex™ adsorbent within this zone hence the net contribution of zone 3 to the adsorption process is zero.

Based on the high level of disturbance brought about by the high pressure liquid jet, the adsorption zone was considered to behave like a continuous stirred tank reactor. Hence the mass balance for adsorption of organic contaminants from grey water onto Nyex™ adsorbent in zone 1 was constructed from Eq. 4.6.

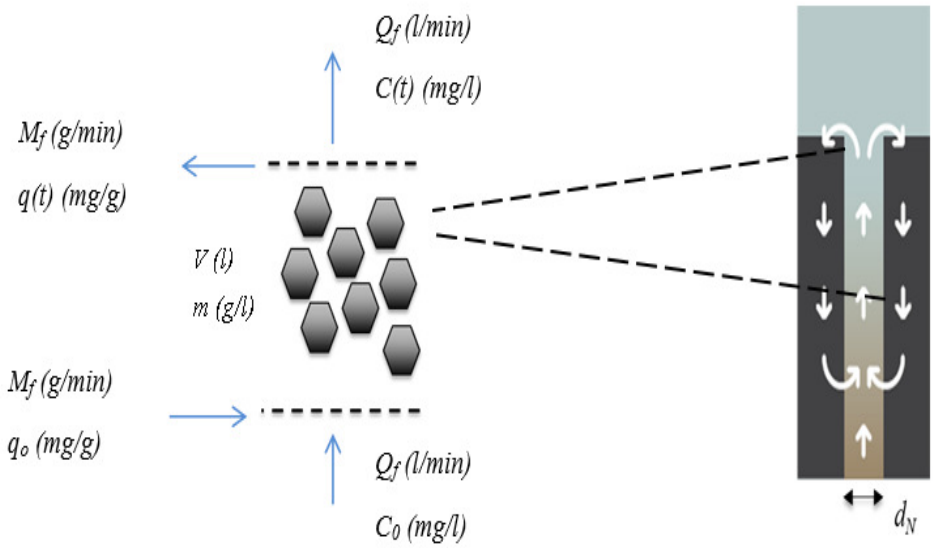


Figure 4.52 - Schematic process occurring in the adsorption zone 1 within the electrochemical cell

The mass balance for a non-reacting compound is:

Rate of accumulation = Rate of inflow – Rate of outflow

Hence,

$$\frac{dC(t)}{dt}\int_V dV = Q_f C_0 - Q_f C(t) \qquad [4\text{-}6]$$

Where C_0 and $C(t)$ in mg/l are the initial concentration and the concentration at time (t), V (l) is the feed volume and Q_f (l/min) is the volumetric flowrate of the grey water solution (Figure 4.52).

The rate of change in grey water concentration in the bulk liquid phase can be described in terms of the rate of adsorption onto the adsorbed phase as shown in Eq.17-6. From performing a batch kinetics and isotherm studies, it was found that the adsorption rate was second order and that the adsorption equilibrium can be described by the Langmuir isotherm (section 15.3). Hence the rate of adsorption at the adsorption zone 1 is given by Eq.4-7.

Pseudo-second order adsorption rate:

$$\frac{dq(t)}{dt} = k_2\left(q_e - q(t)\right)^2 \qquad [4\text{-}7]$$

Where q_e and $q(t)$ are the adsorption capacity in mg/g of adsorbent at equilibrium and at time t, respectively and k_2 is the second-order adsorption rate constant (g mg^{-1} min^{-1}). Langmuir isotherm is described as:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad [4\text{-}8]$$

In which C_e (mg/l) is the bulk liquid concentration at equilibrium, q_m is the maximum monolayer contaminant concentration in the solid phase in mg/g, b (l/mg) is Langmuir adsorption equilibrium constant. Combining Eq.4-7 and 4-8 gives the adsorption rate:

$$\frac{dq(t)}{dt} = k_2\left(\frac{q_m b C_e}{1 + bC_e} - q(t)\right)^2 \qquad [4\text{-}9]$$

At steady state an overall mass balance on organic grey water contaminants in the adsorption zone gives:

In = Out

$$\left(Q_f C_0 + M_f q_{in}\right) = \left(Q_f C(t) + M_f q(t)\right) \qquad [4\text{-}10]$$

Assuming that the adsorbent is fully regenerated prior to each cycle (a cycle refers to the transport of volume of grey water equal to the packed bed volume through the bed) which means q_{in} equals zero, thus Eq.4-10 reduces to:

$$q(t) = \frac{Q_f}{M_f}\left(C_0 - C(t)\right) \qquad [4\text{-}11]$$

Rearranging Eq.4-6 in terms of rate of adsorption gives:

$$\frac{dq(t)}{dt} m_c V = Q_f C_0 - Q_f C(t) \qquad [4\text{-}12]$$

Combining Eq.4-9 and Eq.4-11 to Eq.4-12 yields the overall mass balance equation:

$$V m_c k_2 \left(\frac{q_m b C_e}{1+bC_e} - \frac{Q_f}{M_f}\left(C_0 - C(t)\right) \right)^2 = Q_f \left(C_0 - C(t)\right) \qquad [4\text{-}13]$$

Thus the outlet concentration at time (t) can be determined for a given flow rate and influent concentration (Q_f and C_0), by solving Eq.4-13 if the values of V, k_2, b, q_m, m_c, and M_f are known. The mass flowrate of Nyex™ adsorbent (M_f) can be estimated using Eq.4-14.

$$M_f = u \frac{\pi}{4} d_N \rho_b \qquad [4\text{-}14]$$

Where d_N is the diameter of the regeneration zone and ρ_b is the bulk density of the Nyex™ adsorbent. Because the concentration of Nyex™ adsorbent in g/l at the adsorption zone 1 was unknown and is fairly difficult to determine experimentally, it was assumed that the Nyex™ adsorbent travels with the grey water solution hence Eq.4-15 was used as a first approximation for the Nyex™ adsorbent concentration (m_c). However, the Nyex™ adsorbent is most likely to travel at a lower velocity to the grey water solution as it has a higher density, so it is likely that the first approximation may require some adjustment in order to fit the experimental data.

$$m_c = \frac{M_f}{Q_f} \qquad [4\text{-}15]$$

The kinetics and equilibrium parameters used to solve Eq.4-13 were determined from fitting the pseudo-second order model and the Langmuir isotherm model to the batch experimental data as discussed in section 2.4.3. The concentration of organic contaminants in grey water

solution leaving the packed bed to satisfy Eq.4-13 was estimated using the Solver tool in Microsoft Excel.

Estimated values of Nyex™ concentration (m_c) and mass flowrate of Nyex™ (M_f) in the adsorption zone 1, were obtained by fitting the mass balance model to experimental data obtained at different operating conditions and are detailed in Table 4.8. It can be observed that the mass flowrate of Nyex™ within zone 1 increase from 7 g/s to 20 g/s as the feed flowrate is increased from 10 l/h to 30 l/h. However, no significant change in mass flowrate was observed with an increase in the current density. This was not surprising as the Nyex™ was entrained within the spout, hence it was expected that the mass flowrate of Nyex™ could only be effected by the feed flowrate of the grey water passed through the bed. The increase in mass flowrate of Nyex™ within the adsorption zone observed with increasing flowrate suggests that Nyex™ entrained within the fluid flowing through the spouts/channels was recirculating around the adsorption zone at a higher rate.

Table 4.8 - Estimated mass balance model parameters for adsorption of organic contaminants from grey water onto Nyex™

Q	C0	Charge	M	m
l/h	*mg/l*	*C/g*	*g/s*	*kg/l*
10 l/h	724	90	7	2.58
10 l/h	724	81	6.6	2.4
10 l/h	724	72	6.6	2.38
10 l/h	724	45	6.1	2.2
20 l/h	724	81	14.4	2.5
30 l/h	724	81	20	2.43

It was also noted that the feed flowrate and current density had very little effect on the effective concentration of Nyex™ within the adsorption zone 1. Increasing the charge from 90 C/g to 45 C/g only resulted in a 15% increase in the concentration of Nyex™ available in the adsorption zone. The slight increase in the effective concentration of Nyex™ was due to increase in electrochemical regeneration activities as the charge is increased, which meant more Nyex™ was regenerated over a given period of time. Furthermore, a slight decrease of only 6% in the Nyex™ concentration was observed as the feed flowrate was increased from 10 l/h to 30 l/h.

A non-linear fit of the mass balance model to the experimental data is illustrated in Figure 4.53. The plot shows a reasonably good fit of the model to the experimental data, only at the initial

part of the breakthrough curve. This therefore suggests that the mass transfer model does not provide a good description of the experimental data, probably due to the incorrect assumptions used for formulating the model. For this reason, it was concluded that the mass transfer model cannot be used to predict breakthrough curve.

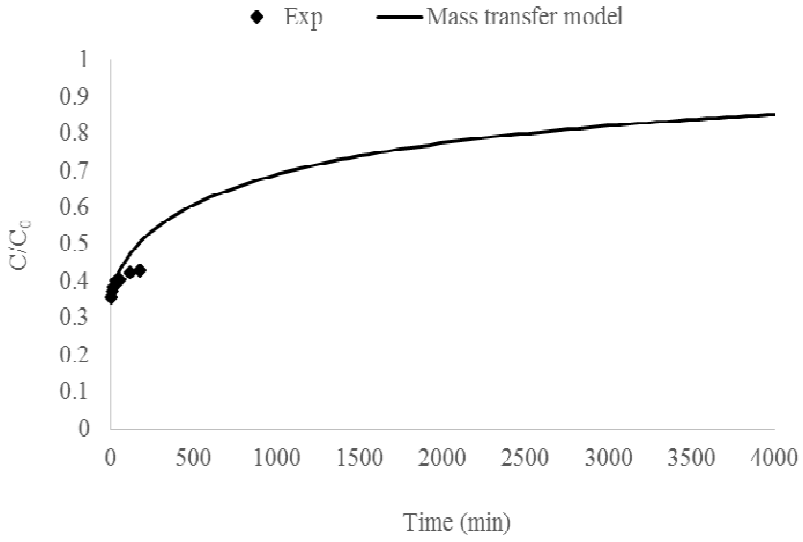


Figure 4.53 - Breakthrough curve: comparison of experimental data with the mass balance model. Experimental data obtained from studies conducted with initial influent COD concentration of 724±80 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm^2

Results from the adsorption models discussed above are summarised below in Table 4.9.

Table 4.9 – Summary of strengths and weaknesses of adsorption models

Model	Strengths	Weaknesses
Dynamic Model		
Yoon-Nelson	* Simple and concise (less parameters required for application) * Provides a suitable description of the experimental breakthrough profile	* Does not include sufficient parameters for design
Adam-Bohart	* Includes important parameters for process design	* Not a suitable fit for the full adsorption profile * More suitable for adsorption with surface reaction * Requires more parameter for application
Thomas	* Provides suitable description of the experimental adsorption profile * Includes important parameters for design	* Requires more parameters for application
Scale-up Model	* Simple and direct mathematical application * Provide useful informtion of the dimensions of the packed bed column	* Does not provide a suitable description of the experimental adsorption profile as only applicable to symetrical breakthrough curves
Mass Balance Model	* Simple and direct mathematical application	* Provides suitable description of the initial part of the experimental adsorption profile only

4.4.3 Breakthrough curve prediction

After conducting an analysis of the different models discussed in the previous sections and evaluating if they corresponded to experimental data obtained using the electrochemical cell. It was found that the Thomas, Yoon-Nelson and mass balance models were the most suitable models for describing the experimental data. However, the Yoon-Nelson model is limited and thus cannot be used to predict the breakthrough curve, and the mass balance model only fitted to the initial part of the experimental data. Hence, the Thomas models was selected and thus utilised in this section to predict the breakthrough curves. Breakthrough curves were predicted at several operating conditions in order to determine the optimum operating parameters for the system.

Influence of the feed flowrate on the breakthrough curve is presented in Figure 4.54. The plot demonstrates that although increasing the feed flowrate increased the breakthrough concentration and reduced the bed exhaustion time, the effect is fairly insignificant. Thus validating the initial assumption that the feed flowrate, and thus the residence time was not the dominating operating parameter. This is due to the fast adsorption of organic contaminants observed as a result of the non-porous nature of the Nyex™ adsorbent. In addition, the plot shows that a reduction in feed flowrate from 50 l/h to 5 l/h did not reduce the breakthrough

time. At a feed flowrate of 5 l/h, a breakthrough concentration of 0.33 can be achieved, this corresponds to a breakthrough concentration of 239 mg/l from an initial feed concentration of 724 mg/l. This breakthrough concentration is still too high compared to the maximum allowable COD limit of 42.8 mg/l required for restricted use of the treated grey water solution. Reducing the feed flowrate further would reduce the breakthrough concentration but at the expense of a very long treatment time.

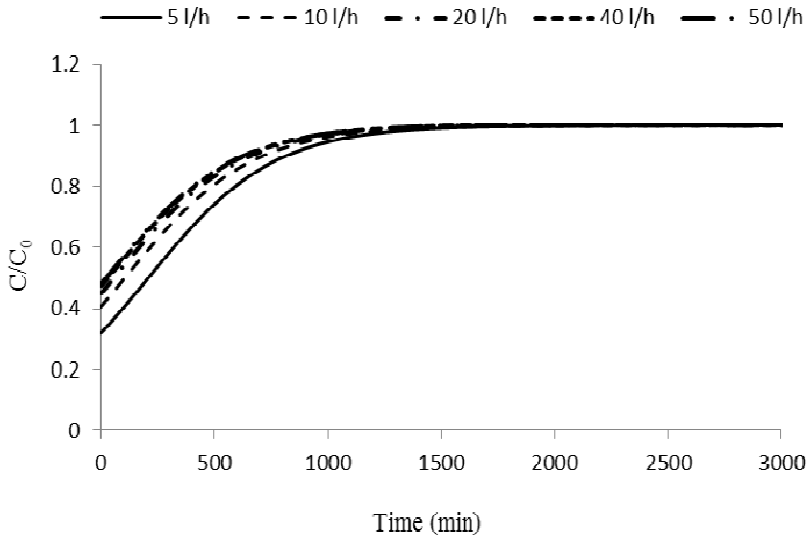


Figure 4.54 - Predicted Breakthrough curve using the Thomas adsorption dynamic model, illustrating the effect of feed flowrate on the removal of organic contaminants from grey water, with initial influent concentration kept constant at 724±80 mg/l and Nyex™ mass of 1.2 kg

A prediction of the breakthrough curve for numerous initial feed synthetic grey water (SGW) concentration was also generated (Figure 4.55). It can be seen from the plot that decreasing the initial feed SGW concentration had negligible effect on the breakthrough concentration as well as the breakthrough time. The plot also shows that the packed adsorbent bed exhaustion time was affected by the change in the initial SGW concentration. As the initial feed concentration is increased from 87 mg/l to 1000 mg/l the exhaustion time decreased from 5280 (88 hours) minutes to over 1140 minutes (19 hours). The breakthrough concentration remained fairly constant at 0.4 for all concentrations evaluated, that corresponds to a breakthrough concentration of 290 mg/l which again is too high for the COD requirement of the treated grey water solution. A further reduction or increase in the feed concentration would according to the model have no effect on the breakthrough concentration.

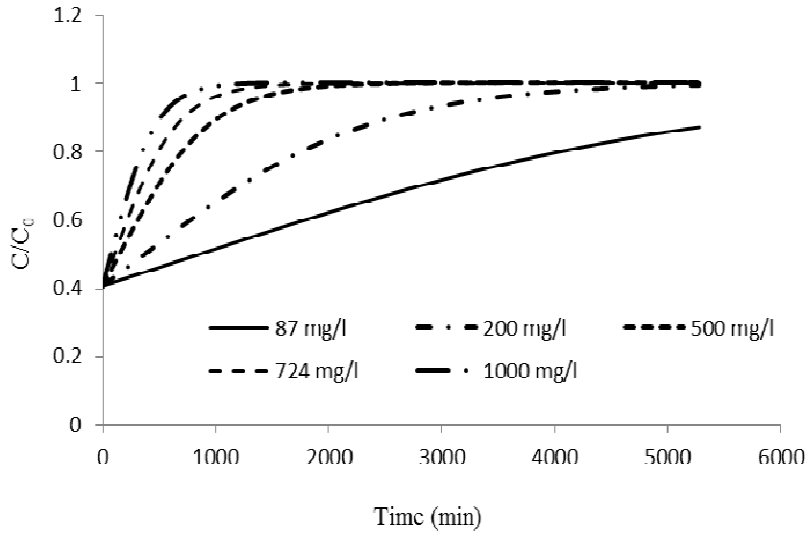


Figure 4.55 - Predicted Breakthrough curve using the Thomas adsorption dynamic model, illustrating the effect of initial influent concentration on the removal of organic contaminants from grey water, feed flowrate kept constant at 10 l/h and Nyex™ mass of 1.2 kg

An investigation of the effects of the mass of Nyex™ on the breakthrough profile was conducted by predicting the breakthrough curve at various Nyex™ mass (1.2, 6, 15, 30, 50 kg). The predicted breakthrough curves depicted in Figure 4.56 shows a significant increase in the breakthrough time and exhaustion time as the mass of Nyex™ is increased. The plot shows that the breakthrough time increased from less than 5 minutes to 3500 minutes (58 hours) as the mass of Nyex™ is increased from 1.2 kg to 50 kg. The bed exhaustion time also increased from 1020 minutes to 5280 with an increase in adsorbent loading from 1.2 kg to 50 kg respectively.

The breakthrough curved shown by the predicted model is very positive, indicating the possibility of achieving very low discharge consent at a minimum adsorbent mass of 15 kg. Using over 15 kg of Nyex™ adsorbent means that the treatment requirement of 28 mg/l and 7.14 mg/l COD concentration for restricted and unrestricted reuse of the treated grey water can be achieved. It also means that the Nyex™ adsorbent can be used for longer to treat a high volume of grey water solution. However, increasing the mass of Nyex™ would mean increasing the size of the system thus reducing the portability of the device for residential use. For instance using 15 kg of Nyex™ would require a bed height of 3.2 m, if the width and length were kept constant.

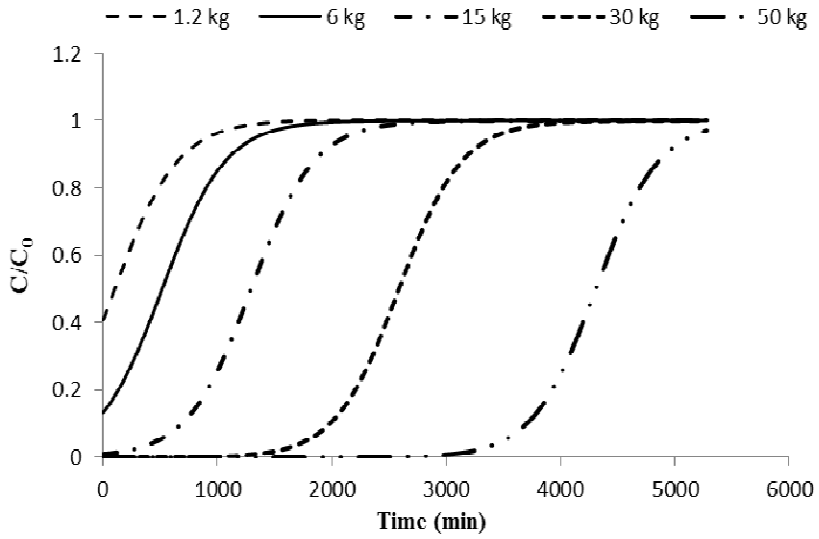


Figure 4.56 - Predicted Breakthrough curve using the Thomas adsorption dynamic model, illustrating the effect of mass of Nyex™ adsorbent on the removal of organic contaminants from grey water, with initial influent concentration and feed flowrate kept constant at 724±80 mg/l and 10 l/h respectively

4.4.4 Implementation of experimental findings

Due to time limitation, it was not possible to fabricate an improved design of the electrochemical cell. However, Arvia™ Technology was able to use some of the data obtained from this work to develop a new design. The system developed by Arvia™ operates in continuous adsorption and regeneration mode, but in this case, the non catholyte unit was used where no NaCl was added to the system (Figure 4.57). The system was operated in reverse current mode in which the direction of the current was varied continuously (in this case every 30 minutes) so that the anode and cathode compartments are switch accordingly. The aim of altering the anode and cathode compartments was to neutralise the pH of the treated water as well as to ensure that organics adsorbed on Nyex™ in the cathode compartment could also be oxidised. The device also utilises a downward flow method to pass wastewater through the packed bed of Nyex™ adsorbent, with the aim of improving the distribution of wastewater throughout the adsorbent bed. To achieve a downward flow without blockage, the flaked Nyex™ particles were replaced with rounded shaped Nyex™ particles to ease the flow of wastewater through the bed.

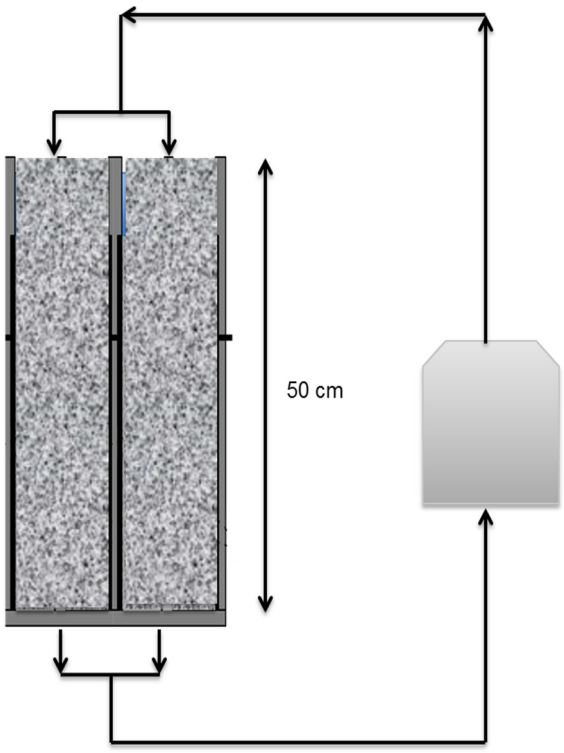


Figure 4.57 - Schematic of the new downwards flow, reverse current system

The system was also operated with continuous recycling of the wastewater solution through the electrochemical cell. The mass of Nyex™ in the cell was increased to 25 kg in the anode compartment and 25 kg of Nyex™ in the cathode compartment. The cell height was increased from 25 cm to around 50 cm and the width of the anode and cathode compartment were also increased to around 5 cm.

During operation of the system, influent grey water was introduced at the top of the cell and the grey water was treated as it flowed down the packed bed of Nyex™ at a range of flowrate of 500 l/h and 250 l/h. Initial feed concentrations of 724 mg/l and 163 mg/l were evaluated with a constant current density of 2 mA/cm^2. Samples were collected from effluent grey water leaving from the bottom of the packed bed and analysed for COD, anionic surfactant and chlorine. The treated grey water was then recycled continuously through the packed bed.

Figure 4.58 and 4.59 shows the level of COD and anionic surfactant respectively, present in the treated grey water over time. The adsorption of organic contaminants onto Nyex™ as expected was very rapid with the majority of the adsorption occurring within minutes, after which the system reached a plateau/equilibrium. The system was able to achieve a 54% and

60% treatment efficiency for COD and anionic surfactants respectively. However, with a Nyex™ mass of 25 kg in the anode and cathode compartment, it was expected based on the Thomas model that up to 100% treatment efficiency should have been achieved. During operation the concentration and flowrate was decreased but this made no difference to the treatment efficiency once the system has reached equilibrium. The low treatment efficiency observed may be attributed to low regeneration efficiency due to insufficient charge available to electrochemically oxidise the level of organic contaminants present in the system. The increased width of the cell could also have led to a reduction in the regeneration efficiency due to the electrodes being further apart, resulting in increased resistance across the bed (Brown et al. 2004b). It has recently been observed after conducting a thorough analysis of the treated solution that electrochemical reduction of the adsorbed organics in the cathode compartment led to the production of an alien organic compound (Brown. N, personal communication, March 2015). The organic by-product accumulated in the treated grey water resulting in the plateau observed in the result, where it appeared no further treatment was achieved.

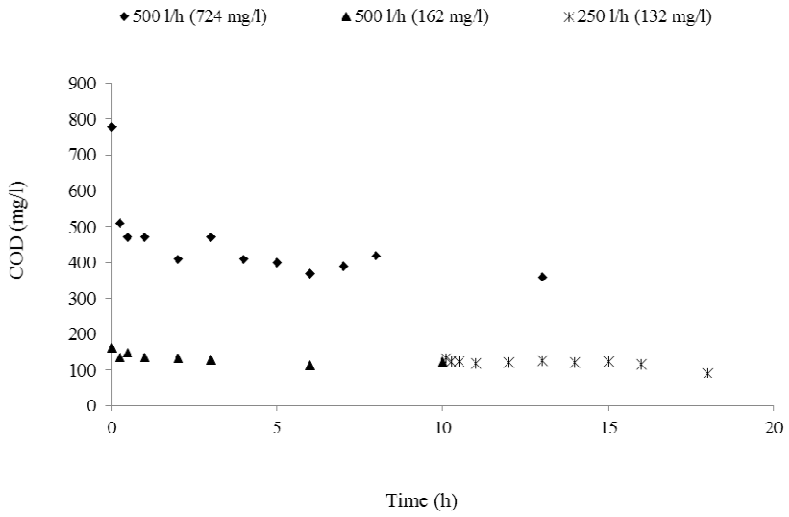


Figure 4.58 - Treatability study; COD concentration in treated grey water solution over time at different operating conditions using the improved downward flow system

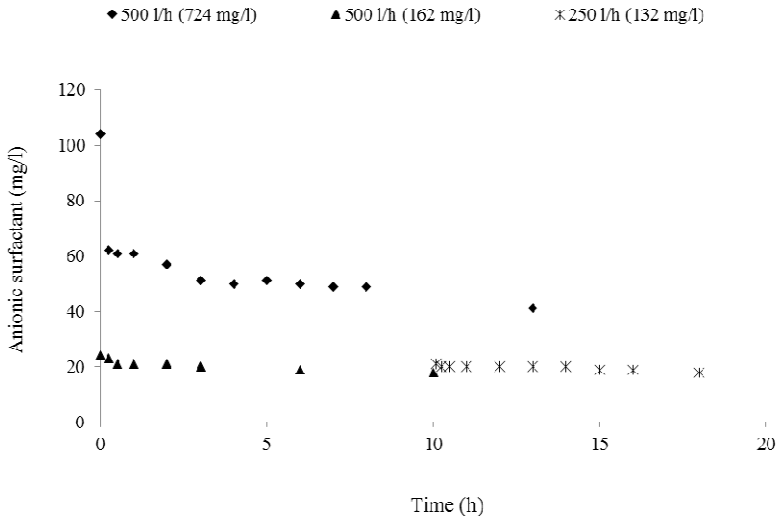


Figure 4.59 - Treatability study; Anionic surfactant concentration in treated grey water solution over time at different operating conditions using the improved downward flow system

4.4.5 Summary

Modelling of adsorption profile

Adsorption dynamic, scale up and mass balance models were fitted to the experimental data obtained from continuous adsorption and electrochemical regeneration using the electrochemical cell. The quality of fit of the model to the experimental data were evaluated in order to determine the most appropriate model for describing the adsorption process occurring within the electrochemical cell.

A linear and non-linear fit of adsorption dynamic models (Adam-Bohart, Thomas and Yoon-Nelson) were used to describe the experimental data as well as to determine important characteristic parameters required for design. It was found that the Adam-Bohart model did not correspond well to the experimental data. It was also observed from the adsorption dynamic models that the adsorption capacity of the packed adsorbent bed increased with an increase in charge passed and a decrease in feed flowrate. It was unfortunately not possible to fit the scale up model to the experimental data. This was due to the fact that the experimental breakthrough curve was non-symmetrical and a symmetrical curve is required for a more accurate estimation of the stoichiometric time.

The mass balance model was developed by assuming that the adsorption of organic contaminants occurred only within the spouts/channels generated as the grey water is pumped through the system. Due to the high level of disturbance within the spouts formed, the adsorption zone was considered to behave like a continuous stirred tank reactor. It was found from fitting the resulting mass balance model to the experimental data that the mass flowrate of Nyex™ recirculating within the adsorption zone increased as the feed flowrate was increased, although no significant effect was observed with changes in the charge passed. It was also observed that the concentration of Nyex™ available for adsorption within the adsorption zone increased with an increase in the charge passed, but decreased as the feed flowrate was increased. The mass balance model appeared to fit well to the initial part of the experimental data, which meant the bed exhaustion time achieved based on the model was different from the exhaustion time obtained from the experiment. It was therefore concluded that the mass balance model was not a good fit for the experimental data and thus could not be used for predicting the breakthrough curve.

Breakthrough curve prediction

The Thomas and Yoon-Nelson models were found to best fit the experimental data. However, because the Yoon-Nelson model is limited in that it does not use characteristic parameters to enable breakthrough curve prediction, only the Thomas model was used to predict the breakthrough curve.

Predicted breakthrough curves for different feed flowrate gave evidence of flow channelling or bed spouting with the breakthrough occurring in less than a minute for all flowrates evaluated. The breakthrough and bed exhaustion time was not significantly affected by changes in the feed flowrate. Breakthrough profiles for different initial concentrations were also predicted using the Thomas model. Again the breakthrough occurred immediately for all initial concentrations evaluated. Although in this case, the bed exhaustion time was shorter with an increase in the initial concentration. For instance, bed exhaustion occurred at 1140 minutes for initial grey water concentration of 1000 mg/l compared to an exhaustion time of 5280 minutes for initial grey water concentration of 87 mg/l. Predicted breakthrough curve for different mass of Nyex™ showed that increasing the mass of Nyex™ improved the breakthrough curve profile with a longer breakthrough time achieved when the mass of Nyex™ was over 15 kg. The increase in the Nyex™ mass appeared to supress the effect of flow channelling resulting in a breakthrough time of 1380 minutes with 30 kg of Nyex™. However, increasing the mass of Nyex™ would reduce the portability of the system.

4.5 Mechanism of Biological Contaminant Removal

4.5.1 Introduction

Results from batch adsorption studies presented in section 4.1.2 provides evidence that microorganisms present in grey water were not adsorbed onto Nyex™, although a reduction in the level of microorganisms was observed. A significant reduction in the level of microorganisms present in the grey water (up to 4-log reduction in microorganism) was also observed during the continuous adsorption and electrochemical regeneration process. In the following section, results from studies undertaken to determine the mechanism of biological contaminant removal from grey water is presented. Three possible mechanisms through which microorganisms can be removed from grey water were suggested:

1. Chlorine disinfection – disinfection of microorganisms either by residual chlorine present in the grey water solution or by chlorine gas and hypochlorite ions generated through electro-chlorination during the electrochemical regeneration process.
2. pH – during the electrochemical regeneration process H+ ions are generated which reduce the pH at the anode compartment to a pH of around 2 to 4.
3. Direct electric destruction – Another possible method is through destruction of microorganisms present in the bulk liquid by electric current.

It is likely that a combination of these process all play a part in removing microorganisms in grey water, but the level of effect these factors have on microorganism removal was not apparent. Trials were therefore conducted by operating the system in both batch and continuous mode and the results are discussed below.

4.5.2 Batch study

The experimental steps employed for the batch adsorption kinetics study was used to evaluate the mechanism of biological contaminants removal in batch adsorption mode. SGW used in this study was formulated using the method recommended by the British Standards Institution as discussed in section 3.1.2. Samples collected in this study were analysed for E.coli and Pseudomonas at United Utilities Laboratory.

4.5.2.1 Effect of residual chlorine present in tap water

Previous tests conducted to investigate adsorption of biological contaminants in the form of E.coli and Pseudomonas in batch adsorption mode showed a slight removal of microorganisms from the grey water (section 4.1.2). Data from the batch study also demonstrated that the reduction in microorganisms observed was not due to adsorption of microorganisms onto Nyex™, but through disinfection by the residual chlorine present in the tap water used for formulating the synthetic grey water (SGW). Further studies were therefore required in order to verify this assumption and determine the effect of dissolved chlorine on microorganism removal in grey water.

Hence studies were carried out to investigate if the level of chlorine present in tap water is sufficient to account for the removal of E.coli and Pseudomonas. In this study, SGW de-chlorinated using sodium thiosulphate and SGW with total chlorine of 1 mg/l were used to conduct batch kinetics studies under similar experimental conditions. It can be seen from the plot in Figure 4.60 and Figure 4.61 that the chlorine present in the tap water used to formulate the SGW was the main source of disinfection leading to the removal of both E.coli and Pseudomonas from the grey water solution. In the de-chlorinated solution, there was barely any reduction in the amount of coliform forming unit (CFU) in the treated SGW. On the other hand a gradual reduction in the CFU was noted in the chlorinated solution with a maximum of 0.1-log removal of both microorganisms noted. It was also observed from the data that the chlorine was used up very quickly and that no further removal of microorganisms occurred after the free chlorine concentration was reduced to below 0.2 mg/l. The reduction in free chlorine was due to degradation by reaction with organic compounds to produce THMs (trihalomethanes) or TCAs (trichloroacetics) in the SGW solution, disinfection of microorganisms in the SGW or has evaporated as the batch system is open.

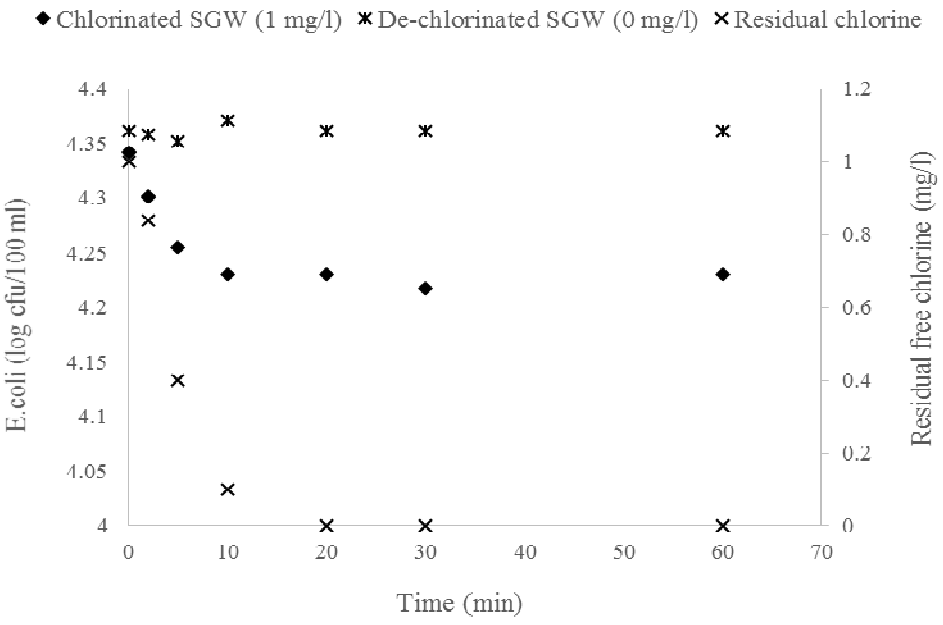


Figure 4.60 - Concentration of E.coli in the bulk liquid phase of the SGW over time, plot demonstrating the effect of residual chlorine present in tap water on E.coli removal; data was obtained using two different SGW both made up with tap water and one of which was de-chlorinated using 2 g/l sodium thiosulfate: test was conducted using SGW volume of 150 ml; 7 g/l Nyex; residual free chlorine concentration in the tap water used was 1±0.25 mg/l; initial E.coli concentration of 10^4 cfu/100 ml and at SGW pH of 6.8±0.5

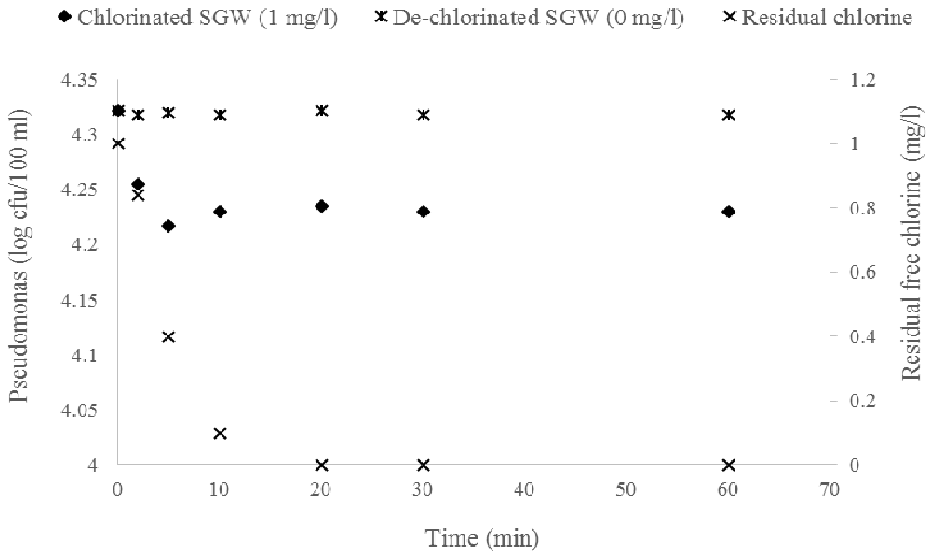


Figure 4.61 - Concentration of Pseudomonas in the bulk liquid phase of the SGW over time, plot demonstrating the effect of residual chlorine present in tap water on Pseudomonas removal; data was obtained using two different SGW both made up with tap water and one of which was de-chlorinated using 2 g/l sodium thiosulfate: test was conducted using SGW volume of 150 ml; 7 g/l Nyex; residual free chlorine concentration in the tap water used was 1±0.25 mg/l; initial Pseudomonas concentration of 10^4 cfu/100 ml; and at SGW pH of 6.8±0.5

4.5.2.2 Evaluation of pH

Tests were also carried out in batch mode to study the effect of pH on the removal of microorganisms from grey water. The study was conducted using de-chlorinated SGW and the pH of the SGW was varied by dosing with 1 M hydrochloric acid until the required pH is achieved. The data generated from this study (Figure 4.62 and 4.63) provide evidence that reducing the pH to below 2 had a significant effect in removing E.coli and Pseudomonas contaminants from the grey water solution. Data from the plot illustrate that at a pH value of 2, the E.coli and pseudomonas present in the SGW was completely destroyed achieving a 4-log removal for both E.coli and Pseudomonas. A 1-log and 0.1-log removal of microorganisms was achieved when the SGW was at a pH of 4 and 6.8 respectively. This suggests that the pH of the SGW or the operating pH of the system is a predominant factor for microorganism removal and complete destruction of E.coli and Pseudomonas can only be achieved at a pH value of below 2. The level of microorganism removal at low pH may be attributed to denaturing of the microorganisms in the acidic environment (Iwasawa et al. 2009).

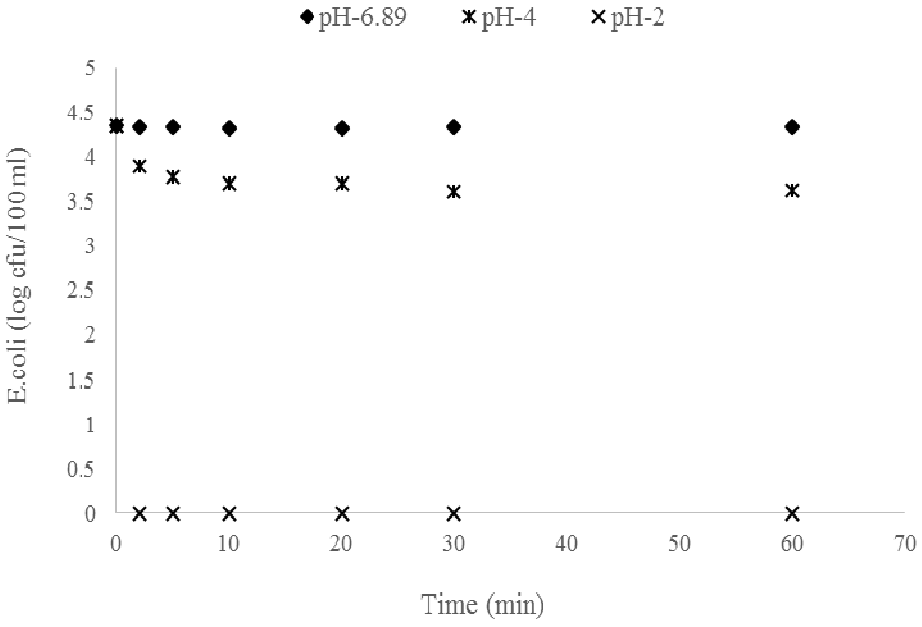


Figure 4.62 - Concentration of E.coli in the bulk liquid phase of the SGW over time, plot illustrating the effect of pH on the removal of E.coli from the SGW; data was obtained using de-chlorinated SGW dosed with 1 M HCl to obtain a pH value between 4 and 2: test was conducted using SGW volume of 150 ml; 7 g/l Nyex; initial E.coli concentration of 10^4 cfu/100 ml and at SGW pH of 6.8±0.5, 4±0.3 and 2±0.1

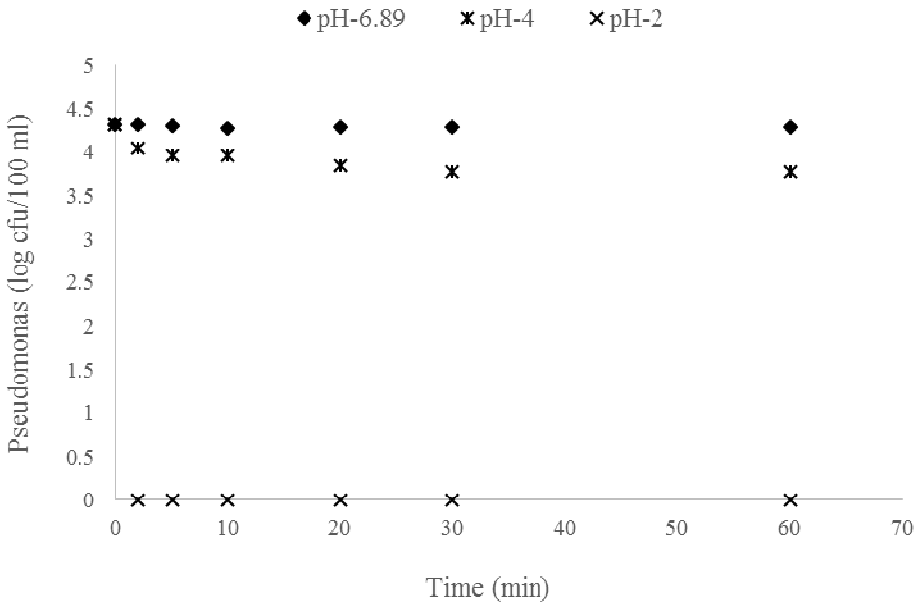


Figure 4.63 - Concentration of Pseudomonas in the bulk liquid phase of the SGW over time, plot illustrating the effect of pH on the removal of Pseudomonas from the SGW; data was obtained using SGW made up with tap water with residual chlorine concentration of 1±0.25 mg/l and dosed with 1 M HCl to obtain SGW with pH value of 4 and 2: test was conducted using SGW volume of 150 ml; 7 g/l Nyex; initial Pseudomonas concentration of 10^4 cfu/100 ml and at SGW pH of 6.8±0.5, 4±0.3 and 2±0.1

4.5.3 Study in continuous mode

4.5.3.1 Direct electric current and electro-chlorination effect

Continuous adsorption and electrochemical regeneration tests were also carried out with SGW formulated from tap water without de-chlorination, using the electrochemical cell. The pH was maintained at approximately 7 using phosphate buffer. Studies were undertaken in order to get some insight into the effect of electro-chlorination on the removal of microorganisms from the grey water. In the data depicted in Figure 4.64 and Figure 4.65, the system was operated with a current density of 2.5 mA/cm^2 and without any current (0 mA/cm^2). The plot indicates that passing current across the cell caused a continuous 4-log reduction in the concentration of E.coli and Pseudomonas when 3% w/v NaCl was used. Whereas without the current and without NaCl, the amount of microorganism in the system increased over time. From the data presented in Figure 4.66 it can be established that the continuous reduction in microorganism observed in the electrochemical cell was due to the production of high concentration of free chlorine, through electrochemical oxidation of chloride ions (electro-chlorination).

Furthermore, a decrease in the CFU value was observed for trials conducted with a current density of 2.5 mA/cm^2 and without the presence of NaCl. Although in this case the system was not able to achieve a 4-log removal of E.coli and Pseudomonas. This suggests that direct electric current had only a minor effect on the removal of microorganisms. It also suggests that the generation of chlorine radicals as well as the high amount of dissolved chlorine generated during electrochemical regeneration in the presence of NaCl, contributed predominantly towards complete removal of E.coli and Pseudomonas from the grey water solution. When 3% w/v of NaCl was added to the system, up to 20 mg/l of free chlorine was generated over 2 hours at an operating current density of 2.5 mA/cm^2 compared to a free chlorine concentration of 1.45 mg/l generated when no NaCl was added. Similar finding was reported by Hussain (2012) for the removal E.coli cells suspended in solution through electrochemical oxidation.

When no current was passed across the cell, the amount of free chlorine in the system decreased to zero from an initial concentration of 2 mg/l and the pH of the system remained at a pH value below 7. In contrast when electric current was passed across the system with 0% w/v NaCl, a 1-log reduction in microorganism was observed. This implies that direct electric current has

some effect on the removal of microorganisms although not as significant as pH or electro-chlorination.

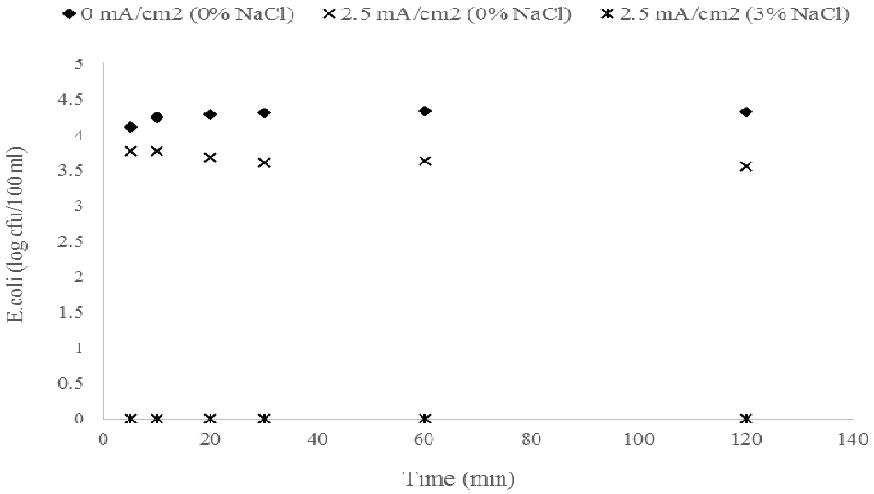


Figure 4.64 - Concentration of E.coli in the bulk liquid phase of the SGW over time, plot illustrating the effect of electro-chlorination on the removal of E.coli from the SGW; data was obtained using two different SGW both made up with tap water and one of which was mixed with 3% w/v NaCl electrolyte: test was conducted using feed flowrate of 10 l/h; initial E.coli concentration of 10^4 cfu/100 ml and at SGW pH of around 7

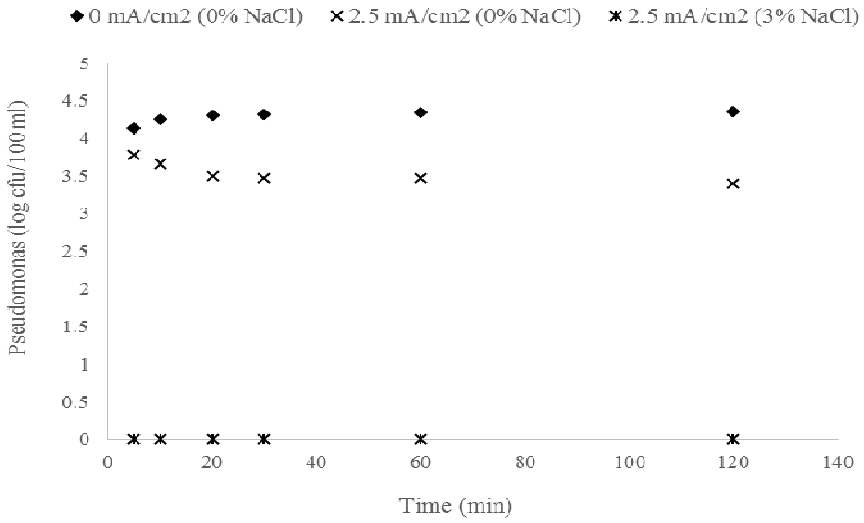


Figure 4.65 - Concentration of Pseudomonas in the bulk liquid phase of the SGW over time, plot illustrating the effect of electro-chlorination on the removal of Pseudomonas from the SGW; data was obtained using two different SGW both made up with tap water and one of which was mixed with 3% w/v NaCl electrolyte: test was conducted using feed flowrate of 10 l/h; initial Pseudomonas concentration of 10^4 cfu/100 ml and at SGW pH of around 7

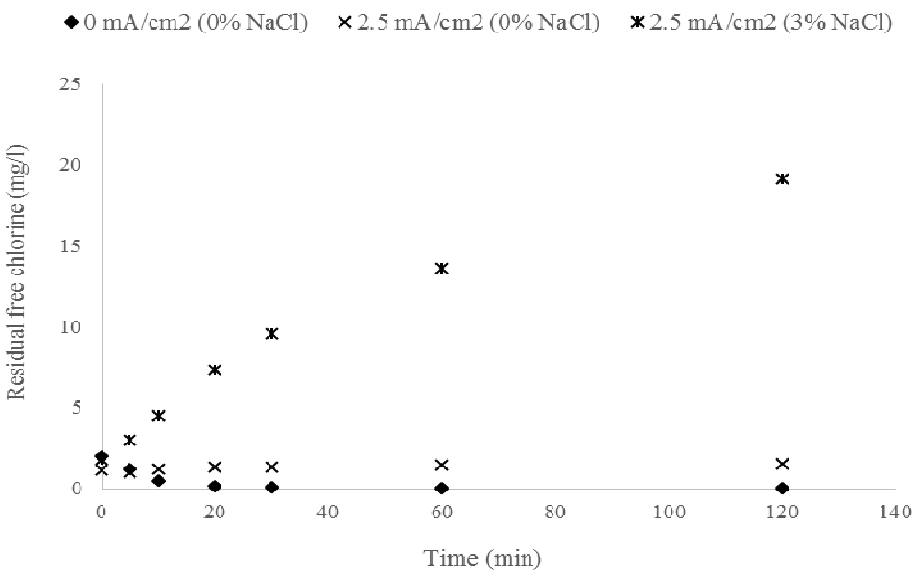


Figure 4.66 - Concentration of free chlorine in the bulk liquid phase of the SGW after electrochemical oxidation reaction: data was obtained using SGW without NaCl and with 3% w/v NaCl: test was conducted using feed flowrate of 10 l/h; initial microorganism concentration of 10^4 cfu/100 ml and at an initial SGW pH of around 7

4.5.3.2 Effect of pH and direct electric current

In order to evaluate the effect of direct electric current on the removal of microorganisms from grey water solution. The SGW solution was de-chlorinated using sodium thiosulphate. The de-chlorinated solution was pumped through the electrochemical cell and tests undertaken with and without current. Data generated from this experiment are shown in the plot in Figure 4.67 and Figure 4.68. The plot indicates that even when no chlorine was present in the solution, the system was still able to remove biological contaminants to an extent and that not passing a current across the cell led to a gradual increase in E.coli and Pseudomonas concentration. This suggests that the increase in pH as a result of electrolysis of water during the electrochemical regeneration process played a part in the destruction of microorganisms.

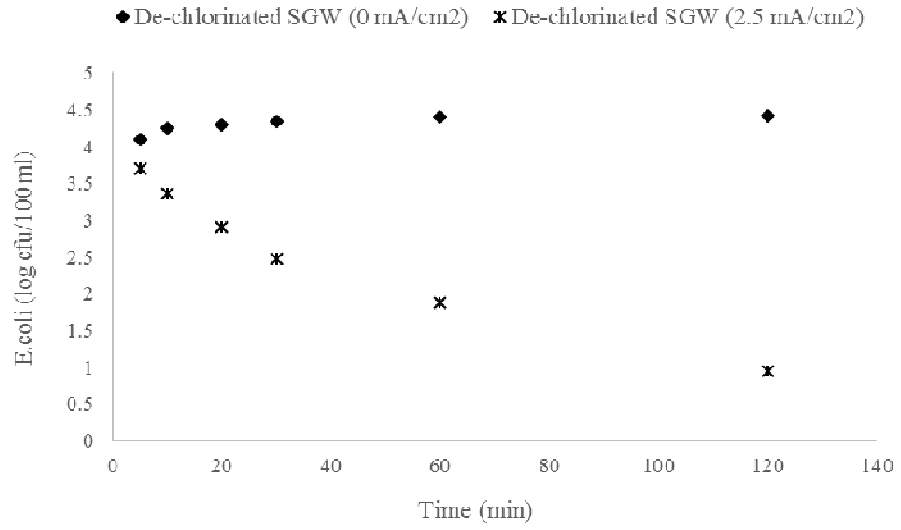


Figure 4.67 - Concentration of E.coli in the bulk liquid phase of the SGW over time, plot obtained from test undertaken to investigate the effects of direct electric current on the removal of E.coli; data was obtained using de-chlorinated SGW which was de-chlorinated using 2 g/l sodium thiosulfate; test was conducted at feed flowrate of 10 l/h; initial E.coli concentration of 10^4 cfu/100 ml and at an initial SGW pH of 6.8±0.5 which decreased to pH of around 2 during electrochemical regeneration

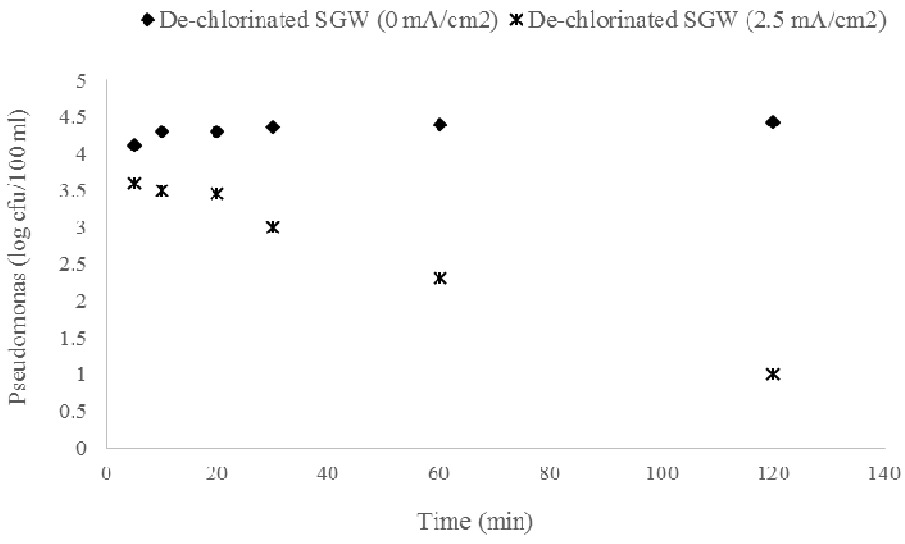


Figure 4.68 - Concentration of Pseudomonas in the bulk liquid phase of the SGW over time, plot obtained from test undertaken to investigate the effects of direct electric current on the removal of Pseudomonas; data was obtained using de-chlorinated SGW which was de-chlorinated using 2 g/l sodium thiosulfate; test was conducted at feed flowrate of 10 l/h; initial Pseudomonas concentration of 10^4 cfu/100 ml and at an initial SGW pH of 6.8±0.7 which decreased to pH of around 2 during electrochemical regeneration

4.5.4 Summary

Studies to investigate the mechanisms of microorganism removal from grey water were carried out in both batch and continuous mode, and results were presented and discussed in this chapter. Batch experimental studies demonstrated that a 0.1-Log reduction of both E.coli and Pseudomonas can be achieved. This reduction was attributed to the presence of residual chlorine in the tap water used to formulate the SGW. Test carried out to investigate the effect of pH showed complete destruction of E.coli and Pseudomonas with a 4-log reduction achieved in both case at a pH value of 2. At a higher pH value of 4, a 1-log reduction was observed.

Operating the system in continuous mode using the electrochemical cell, studies were undertaken to evaluate the effect of electro-chlorination on microorganism removal. Results obtained from this study suggested that the electro-chlorination process had a significant effect on the removal of microorganisms.

A 4-Log reduction was achieved for E.coli and Pseudomonas, only when a free chlorine concentration of 3 mg/l was generated. It was also found that direct electric destruction also played a role although further studies are required to verify this result.

In general, it can be concluded that electro-chlorination and low pH were the main mechanisms through which microorganisms can be removed from SGW using this technique. These parameters are related, as more free chlorine is generated at low pH which also provides additional disinfection potential.

4.6 Estimate of Insulation Requirement and Design of Heat Recovery Unit

4.6.1 Introduction

Heat loss from water leaving the bathroom as it travelled through the system was evaluated by installing thermocouples around the insulated pilot scale unit, which was connected to the shower/bath drainage system at the Energy House. The heat energy lost around the system was estimated using basic heat loss equations as detailed in Coulson et al. (1996) and was compared to readings taken from the thermocouples in order to determine if the system was properly insulated. The aim of this calculation was to provide an estimation of the maximum temperature lost and thus gauge how efficient the system was at retaining the heat energy in the water. Section 4.6.2 provides an example of steps used to calculate the heat loss around the feed tank and the pipe fittings, similar methods were also used to determine the heat energy lost as the water passed through the electrochemical cell. The insulation requirement was subsequently estimated in section 4.6.2.3, this is followed by an evaluation of a possible design for a heat recovery unit (4.6.3).

4.6.2 Estimate of heat lost

4.6.2.1 Heat balance around tank

Because the feed tank was not completely filled with water, the total heat loss from the tank (Q_{Tot}) was calculated as the sum of the heat loss on the wet and dry side. Heat lost from each sides of the cylinder tank was calculated as follows:

The wet cylinder side $$Q_w = U_w \times A_w \times (T_L - T_A)$$

The wet base side $$Q_b = U_b \times A_b \times (T_L - T_A)$$

The dry cylinder side $$Q_d = U_d \times A_d \times (T_V - T_A)$$

The dry roof side $Q_r = U_r \times A_r \times (T_V - T_A)$

The total heat loss $Q_{Tot} = Q_w + Q_d + Q_r + Q_b$

Where U is the overall heat transfer coefficient, A is the heat transfer area, T_L is the wet wall temperature, T_V is the dry wall temperature and T_A is the atmospheric temperature.

The total overall heat transfer coefficient (U_T) equation is built up of a combination of the heat transfer coefficient on the inside of the tank, the conductive heat through the tank wall/insulation and the heat transfer on the outside of the tank for the wet and dry side of the tank. For example, the following equation was used to calculate the overall heat transfer coefficient for the wet wall side of the tank:

$$\frac{1}{U_w} = \frac{1}{h_w} + \frac{x_w}{k_w} + \frac{1}{h_{Aw} + h_R} \qquad [4\text{-}16]$$

Where h_w is the heat transfer coefficient on the inside wall (W/m^{2}K), the second part of the equation describes the conductive heat loss through the wall of the tank and or insulation; x_w is the thickness of the tank (m) and k_w is the thermal conductivity of the tank (W/mK). The last part of the equation describes the heat transfer on the outside of the tank and is a sum of the heat loss through radiation, h_R, and convection, h_{Aw}.

The heat transfer coefficient was calculated by means of Nusselt's relation for horizontal and vertical tank surfaces:

$$N_{Nu} = \frac{hL}{k} \Rightarrow h = \frac{N_{Nu}k}{L} \qquad [4\text{-}17]$$

Where k is the thermal conductivity of the fluid and L is the effective length or diameter of the surface and h is the heat transfer coefficient.

The total overall heat transfer coefficient was calculated as 9.320 W/m^{2}K which corresponds to a heat loss of 159 W for the un-insulated tank over a surface area of 2.15 m^2. This means that around 3.82 kWh is lost from the tank per day, which implies to around 115 kwh per month.

Time taken for the water temperature to drop to a specific temperature T_{final} was calculated using:

$$t = \ln \frac{(T_A - T_{initial})}{(T_A - T_{final})} \times \frac{m_w c_p}{U_T A_T} \quad [4\text{-}18]$$

Where;

t = time taken for temperature drop

T_A = atmospheric temperature

$T_{initial}$ = initial temperature of water in tank

T_{final} = final temperature of water in tank

m_w = Mass of water in tank

c_p = specific heat capacity of water

U_T = total overall heat transfer coefficient

A_T = total surface area of tank

The estimated time taken for the water temperature in the tank to drop from 46 to 45°C (temperature drop of 1°C) was estimated at 11.56 minutes, which corresponded well with reading taken from the thermocouple. This temperature drop is not significant if the heat energy is to be recovered immediately.

4.6.2.2 Heat balance around pipe

The total heat transfer coefficient along the pipe per unit length was calculated as:

$$\frac{1}{U_T} = \frac{1}{h_i \times \pi d} + \frac{x}{k \times \pi d_o} + \frac{x_i}{k_i \times \pi d_{oi}} + \frac{1}{h_o \times \pi d_o} \quad [4\text{-}19]$$

Where h_i is the heat transfer coefficient inside the pipe. The second and third part of the equation describe the conductive heat transfer through the pipe wall and insulation respectively; h_o is the total heat transfer coefficient on the outside of the pipe and is a combination of the heat loss through radiation and convection. The estimated heat loss showed that heat loss along the pipe should be less than 1°C. However, the data collected from the thermocouple showed a heat loss of around 3°C, which was most likely due to losses as the water passed through the pump and filter. This therefore indicates that the majority of the heat loss took place around the pump and filter where an additional temperature drop of around 2°C was noted. This heat loss is not too significant and can be controlled by improving insulation around the pump and the filter.

4.6.2.3 Estimation of insulation thickness

Steady state, one dimensional heat flow through insulation system is governed by Fourier's law:

$$Q = -k_i A \frac{dt}{dx_i} \qquad [4\text{-}20]$$

Where:

Q = rate of heat flow

A = cross sectional area normal to heat flow

k_i = thermal conductivity of insulation material

$\frac{dt}{dx_i}$ = temperature gradient

For a cylindrical tank, the above equation can be integrated and rearranged as follow:

$$Q = k_i A \frac{T_{Bulk} - T_{surf}}{r_i \ln\left(\frac{r_i}{r_o}\right)} \qquad [4\text{-}21]$$

Where A is the outer surface area and r_o and r_i are the outer and inner radius respectively. The term $r_i \ln\left(\frac{r_i}{r_o}\right)$ is the equivalent thickness of the insulation layer. Hence rearranging Eq.19-6 in terms of the equivalent thickness of the insulation layer gives:

$$Q = k_i A \frac{T - T_{surf}}{x_i} \qquad [4\text{-}22]$$

As mentioned earlier, the heat transfer from the surface is a combination of convection and radiation. The heat loss from the surface is calculated as:

$$Q_{surf} = h_o A\left(T_{surf} - T_A\right) \qquad [4\text{-}23]$$

To determine the thickness of the insulation layer required to control the surface temperature T_{surf} to a certain value given the bulk liquid and the atmospheric temperature. It was assumed that at steady state, the heat flux through the insulation to the outside surface (Q_{ins}) equals the heat flux from the surface to the ambient air (Q). That is:

$$Q = Q_{surf}$$

$$kA\frac{T - T_{surf}}{x_i} = h_o A\left(T_{Surf} - T_A\right) \qquad [4\text{-}24]$$

Rearranging Eq.19-9 in terms of the equivalent thickness of the insulation layer gives:

$$x_i = \left(\frac{k}{h_o}\right)\frac{T - T_{surf}}{T_{surf} - T_A} \qquad [4\text{-}25]$$

The equivalent insulation thickness required to keep the surface temperature below 25°C was estimated at 19 mm for an insulation with thermal conductivity of 0.04 W/mK and 9.3 mm for insulation with thermal conductivity of 0.02 W/mK. The higher the thermal conductivity, the thinner the insulation required, using a thinner insulation material means the system is not too bulky. However, the thinner the insulation material the higher the cost of insulation, and this has to be considered when selecting an insulation material. Table 4.10 provides a list of

insulation required to keep the water in the tank at 46°C for at least 21 minutes in order to enable an economical decision in selecting the appropriate insulation.

Table 4.10 - Estimated heat loss and insulation requirements

Thermal conductivity (W/m^2K)	Estimated insulation thickness (mm)	Heat loss (J/s)	Cooling time from 46°C to 45°C (min)
0.02	9.31	70.1	21
0.04	18.63		
0.045	20.95		

4.6.3 Proposed design of heat recovery unit

Heat recovery from the grey water was evaluated based on heat recovery from the drainage pipe close to the shower. At this point, the grey water temperature was at its maximum of 49°C. A drainage pipe heat recovery (DPHR) unit was considered instead of a storage heat recovery unit because it has a smaller footprint and does not require sterilisation. Recovering the heat as close as possible to the shower drainage pipe will maximise the heat transfer rate. Basic heat exchanger equations was used to estimate the heat transfer rate using the parameters detailed in Table 4.11. The temperature of the grey water and mains water at various points in the system were determined experimentally, the dimension of the drainage pipe was also known. However, the dimensions of the heat recovery coil were unknown and were estimated using the method described by Patil et al. (1982) (APPENDIX E). The design was conducted using a range of preselected mains water outlet temperatures, from this, the mass flowrate of the mains water and the warm water outlet temperatures were also estimated.

In the drainage pipe heat recovery system a vertical section of the plastic drain pipe can be replaced with a conducting copper pipe of similar size, with a second copper pipe wrapped tightly around the vertical pipe. It was also assumed that warm grey water drains down the internal wall of the vertical pipe, while cold mains water circulates up through the coiled pipe as depicted in Figure 4.69. It was assumed that the temperature of the grey water was 49°C as it enters the drain, the design was conducted with a mains water temperature of 8°C. Various forms of drainage pipe heat recovery device are readily available to purchase. The aim of this calculation is therefore to determine the coil dimensions or area to achieve the required

duty/heat transfer rate. The following steps were taken to determine the dimensions of the heat recovery system:

To enable the design, the required duty (Q) and outlet mains water temperature was initially estimated. The duty required to enable an increase in the mains water temperature (T_{iC}) from 8°C was estimated as:

$$Q_C = M_C \times c_{pC} \times (T_{oC} + T_{iC}) \quad [4\text{-}26]$$

To calculate the grey water outlet temperature (T_{oH}) at different mains water outlet temperatures (T_{oC}), an energy balance was carried out around the system.

Heat lost from the warm grey water (hot stream)

$$Q_H = M_H \times c_{pH} \times (T_{iH} + T_{oH}) \quad [4\text{-}27]$$

Heat energy gained by the cold mains water

$$Q_C = M_C \times c_{pC} \times (T_{oC} + T_{iC}) \quad [4\text{-}28]$$

Once the grey water and mains water are passed through their respective pipes, the heat energy which flows from out of the warm grey water equals the heat energy which flows into the cold mains water, hence the overall energy balance equation becomes:

$$Q_C = Q_H \quad [4\text{-}29]$$

Hence the outlet grey water temperature was estimated as:

$$T_{oH} = T_{iH} + \frac{M_C (T_{oC} - T_{iC})}{M_H} \quad [4\text{-}30]$$

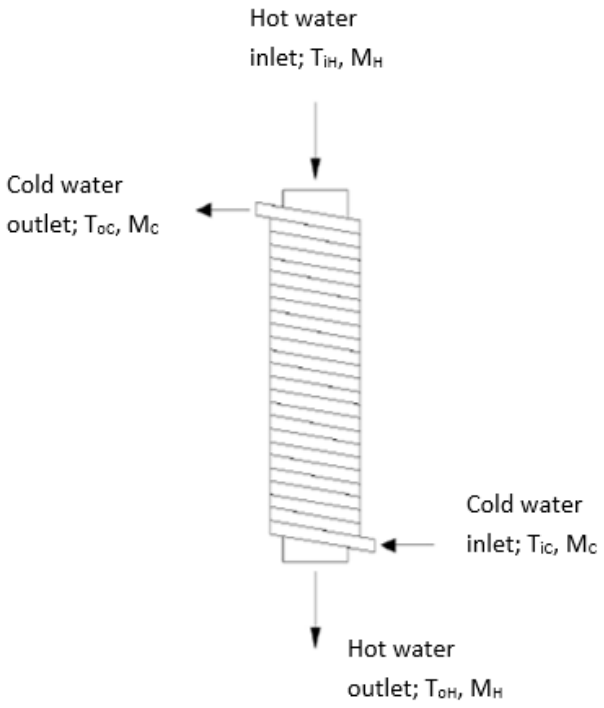


Figure 4.69 - Schematic of the drainage pipe heat recovery system illustrating the flow direction of the warm and the cold streams

The overall heat transfer coefficient was estimated at 249 W/m^{2}K using the method described by Patil et al. (1982). The higher the overall heat transfer value, the higher the level of heat recovery. It was noted that the overall heat transfer value was only affected by the thickness of the coil, rather than the diameter. Hence during the design calculation, the lowest possible coil thickness was selected as detailed in Table 4.11.

Table 4.11 - Parameter used for designing the drainage pipe heat recovery unit; the outer diameter of the coil was estimated as half the diameter of the drain pipe, the inside diameter of the coil was calculated to obtain a minimum coil thickness value for better heat transfer

Fluid Properties		
Symbol	***Description (unit)***	***Value***
T_{iH}	Inlet grey water temperature (°C)	49
T_{iC}	Inlet mains water temperature (°C)	8
M_H	Mass flowrate of grey water (kg/h)	181
ρ	Density (kg/m3)	1000
μ	Viscosity (mPa.s)	0.658
c_p	Specific heat capacity of water (kJ/kg °C)	4.183
k_f	Heat transfer coefficient of water (W/m °C)	0.6
Pipe properties		
Symbol	***Description (unit)***	***Value***
dip	Inside vertical pipe diameter (m)	0.04
B	Outside vertical pipe diameter (m)	0.04826
D	Inside coil diameter (m)	0.016087
D_H	Average helix diameter (m)	0.056303
d_o	Outside coil diameter (m)	0.02413
D_1	Inside diameter of helix (m)	0.068368
D_2	outside diameter of helix (m)	0.044238
k_c	Heat transfer coefficient of copper (W/m °C)	388

The estimated overall heat transfer coefficient was then used to estimate the heat transfer surface area by rearranging the heat transfer equation as follows:

$$Q = UA\Delta T_m \qquad [4\text{-}31]$$

Rearranging in terms of heat transfer area gives:

$$A = \frac{Q}{U\Delta T_m} \qquad [4\text{-}32]$$

Where T_m is the log mean temperature difference and for a counter flow system, T_m is expressed as:

$$\Delta T_m = \frac{(T_{iH} - T_{oH}) - (T_{oH} - T_{iC})}{\ln\left[\frac{(T_{iH} - T_{oC})}{T_{oH} - T_{iC}}\right]} \qquad [4\text{-}33]$$

Once the heat transfer area was determined, the number of coils and the required coil length was then calculated (APPENDIX E). The plot in Figure 4.70 provides an illustration of the length of coil required for different mains water outlet temperature (T_{oC}) and flowrates (m_C). From the plots, it appears that the length of the coil is greatly affected by the required mains water outlet temperature and the mains water flowrate. As the outlet mains water temperature and mass flowrate of the mains water increased, the estimated heat transfer area also increases. At a high mains water mass flowrate of 3 kg/min, the mains water temperature can only be increased to a maximum of 20°C whilst passing the mains water at a lower mass flowrate of 0.3 kg/min enabled an increase in mains water temperature of over 45°C.

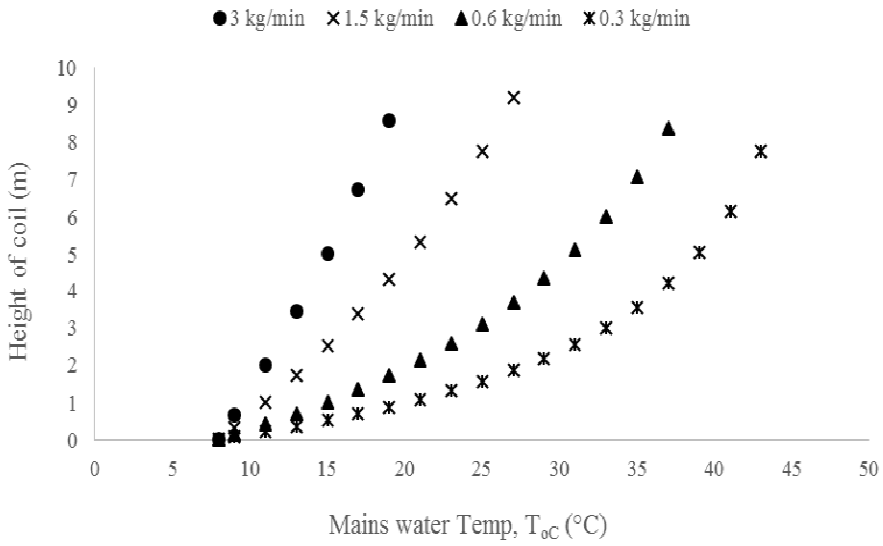


Figure 4.70 - Heat recovery design; plot illustrating the required coil height against mains water outlet temperature at a range of mains water mass flowrate. Design based on heat recovery from the shower/bath drainage pipe by passing cold mains water through a copper pipe wrapped around the drain pipe

As expected, a longer coil length means more heat can be recovered as the heat transfer area is increased. However, it may not be possible to increase the length of the coil above 3 metres depending on the property where the device is installed. Hence, it appears from the plot that the highest possible mains water outlet temperature which can be achieved from the system is 30°C, this was observed at a coil length of 3 metre and a mains water mass flowrate of 0.3 kg/min. For a more modest operation, in which the length of the coil is 1 metre and the mass flowrate of the mains water is 0.3 kg/l, it may be possible to increase the incoming mains water temperature to 20°C.

4.6.4 Summary

Heat energy lost throughout the system was investigated. The calculation showed that very little heat was lost as the warm water flowed through the pipes, however reading from the thermocouples installed around the system suggests that the majority of heat was lost at the pump and filter. It was also concluded from the calculations that it is possible to have the warm water stored with negligible heat loss for over 20 minutes as long as the storage tank is properly insulated. The estimated temperatures corresponded very well with the actual values taken from the installed thermocouples, which confirms that the temperature lost around the system can be estimated using the heat loss equations used. Based on the insulation calculations, an insulting material with a high thermal conductivity is required to avoid the unit being too bulky. However, insulation materials with high thermal conductivity are often more costly. On the other hand, if the heat recovery was carried out at the drainage pipe close to the shower/bath, there would be less need to insulate the system. A higher heat transfer rate can also be achieved if there is a greater temperature difference between the warm water and the cold mains water. Design of a drainage pipe heat recovery unit demonstrated that it is possible to increase the mains water temperature from 8°C to 30°C, but a coil length of 3 metre is required with a mains water mass flowrate of 0.3 kg/min.

4.7 Analysis of Cost and Economical Benefits

4.7.1 Introduction

The economics (i.e. the cost to consumers and the cost benefits for consumers) is a very important driver. The system can only be economically feasible if the cost saved by consumers (cost savings) is greater than the cost expended (operating cost). The economic feasibility of the system was investigated by evaluating the operating cost of the system as well as possible savings from water and heat energy recovery.

4.7.2 Average daily grey water generation capacity

Grey water generated from bathroom usage was used as the main source in this project, the cost estimation was based on the capacity of grey water generated by an individual. An estimation of the level of water usage (Y_G), was calculated using the equation ((Department for Communities and Local Government, 2009) :

$$Y_G = \delta \sum \left[(Sh \times t_{sh} \times F_{sh}) + (B \times F_b) + (H \times t_{wb} \times F_{wb}) \right] \quad [4\text{-}34]$$

Where; δ is the number of individuals/users

Sh is the average flow-rate from the shower in liters per minutes (l/min)

t_{sh} is the average length of time in shower in minutes (min)

F_{sh} is the frequency of usage for the shower

B is the bath volume to overflow unoccupied in liters (l)

F_b is the frequency of usage for the bath

H is flow-rate from taps for the wash basin in liters per minutes

t_{wb} is the average length of time tap is used in minutes (min)

F_{wb} is the frequency of usage for the wash basin

For calculating the volume of water consumed by a single person, it was assumed that the individual spends around four minutes in the shower and uses the wash basin for a total of 1 minute once a day. It was also assumed that the user only showers once a day (thus F_{sh} equals

one) and F_b was taken from the water efficiency calculator (Department for Communities and Local Government, 2009). The average water usage in the bathroom was calculated as:

$$(10.9\times4\times1)+(150\times0.11)+(10\times1\times1)=70 \text{ l/person/day}$$

Hence an estimation of the operating cost as well as the cost generated from water and heat recovery was established on a total grey water volume of 70 litres per person per day.

4.7.3 Operating cost

The operating cost of the unit consists mainly of the electric cost required for electrochemical regeneration of the Nyex™ adsorbent and the cost of pumping the grey water around the system. The operating method of the system has not yet been confirmed as more work is required to develop the electrochemical cell. Hence it was assumed that with an operating flowrate of 17.5 to 20 l/h and grey water capacity of 70 litres, the system can be operated in continuous adsorption and electrochemical regeneration mode for 4 hours. An operating current density of 14.4 mA/cm^2 was selected as it was found to provide effective regeneration of the adsorbent (section 16.2). At this current density, the system was able to achieve a treatment efficiency of 57% of grey water with initial COD concentration of 724 mg/l. It was also assumed that after continuous adsorption and electrochemical regeneration for 4 hours, batch electrochemical regeneration was conducted for 50 minutes at a current density of 14.4 mA/cm^2 (which is equivalent to 22 C/g) to ensure complete regeneration of Nyex™. In general, electrochemical regeneration would take place over a 4 hours 50 minutes or 5 hours and the pumps would be in operation for a total of 4 hours.

4.7.3.1 Electrochemical regeneration

With a current of 9A (equivalent to current density 14.4 mA/cm^2) passed across the electrochemical cell and a corresponding voltage of 9.2 V, It was assumed that the regeneration of the adsorbent will take place during the 4 hours operating time and another 1 hour of batch electrochemical regeneration to ensure full regeneration of the adsorbent. Hence, the total electrochemical regeneration time was 5 hours (calculation is for once through cycle only, and does not take recycling into account). Thus the amount of energy used to regenerate the Nyex™ adsorbent equates to 0.42 kWh.

The estimated cost was based on grey water with initial COD of 724 mg/l, the COD for bathroom grey water is often lower than this, especially if the user spends more time in the shower resulting in a more diluted solution. This means that the operating cost from electrochemical regeneration would decrease as less current is required to regenerate the adsorbent due to the lower level of organics present.

4.7.3.2 Pumping

There were two pumps used in the system, one for pumping the grey water from the bathroom to the feed/storage tank and another used for pumping the grey water from the feed tank through the electrochemical cell.

The grey water leaving the bathroom was assumed to be pumped at a flowrate of 15 l/min which was selected as it was slightly higher than the average flowrate of a shower, and the head difference was set at 1.5 meters. The power (P) required for pumping was estimated using the equation:

$$P = Q_f \rho g H \qquad [4\text{-}35]$$

Where Q_f (m^3/s) is the flowrate, ρ (kg/m^3) is the fluid density, g (m/s^2) is the acceleration due to gravity and H (m) is the head difference. Hence the estimated power required for pumping the grey water from the bathroom to the feed tank was 0.004 kWh

The power required to pump grey water through the cell was calculated as described below. The bed volume fraction and Reynolds number was initially calculated using Eq.4-36 and 4-37, respectively.

$$\varepsilon = 1 - \frac{m}{A_c h \rho_p} = 1 - \frac{1.2}{(0.28 \times 0.02) \times 0.75 \times 412} = 0.31 \qquad [4\text{-}36]$$

$$\mathrm{Re} = \frac{u \rho d_p}{\mu(1-\varepsilon)} = \frac{0.000409 \times 1000 \times \left(450 \times 10^{-6}\right)}{0.001 \times (1 - 0.31)} = 0.27 \qquad [4\text{-}37]$$

Since the Reynolds number is below 10, the pressure drop was estimated using the Carman Kozeny equation.

$$\frac{-\Delta P}{h} = 180\frac{\mu u}{d_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3} = \left(180\times\frac{0.001\times 0.000409}{(450\times10^{-6})^2}\times\frac{(1-0.31)^2}{0.31^3}\right) = 5810 \text{ pa/m}$$

$$-\Delta P = 5810\times 0.75 = 4357 \text{ pa} \quad [4\text{-}38]$$

Hence the power required to pump the grey water through the packed bed was estimated as:

$$P = Q\times\Delta P = 0.000167\times 4357 = 0.73 \text{ W} = 0.003 \text{ kWh} \quad [4\text{-}39]$$

Hence the total energy used per day for pumping the grey water through the system and for electrochemical regeneration is 0.43 kWh. Based on a treatment capacity of 70 l/day and an energy cost of £0.15/kWh (Southern Electric, 2015), the total operating cost per year was estimated as:

$$\left(\frac{70\times365}{1000}\right)\frac{m^3}{yr}\times\left(\frac{0.43}{70/1000}\right)\frac{kWh}{m^3}\times£0.15/kWh = £24/yr \quad [4\text{-}40]$$

4.7.4 Cost savings

The cost savings is realised from reduced mains water use as well as reduced volume of water going to sewerage, which means lower water and sewerage cost. There is also cost savings from heat recovery which was also considered in this section.

4.7.4.1 Water and sewerage

The treatment capacity of the system was assumed to be an average of 70 l/day, this means that the amount of water used and sent to sewerage could be reduced by 70 l/day. Hence, based on a daily usage of 70 l/h and a water and sewerage charge of approximately £1.20/m^3 and £2.30/m^3 respectively (Southern Water, 2015), the cost savings was calculated as follow;

Water saving

$$\left(\left(\frac{70\times365}{1000}\right)m^3\right)\times£1.20/m^3 = £30.66/yr \quad [4\text{-}41]$$

Sewerage saving

$$\left(\left(\frac{70\times365}{1000}\right)m^3\right)\times£2.30/m^3 = £58.76/yr \quad [4\text{-}42]$$

This means around £89.42 could be saved per year from water recycling alone. It is important to note that the estimated cost savings does not take into account purging and assumed all recycled water is used which may not always be the case. Taking these factors into account would reduce the amount of water recycled and thus reduce the savings per year.

4.7.4.2 Heat recovery

The energy required to heat the water is determined from the specific heat relationship ($Q = c_p m\Delta T$). The heat recovery was evaluated in chapter 19, assuming that the mains water was preheated from 8°C to 25°C as discussed in chapter 19. It was also assumed that the preheated water was immediately pumped to an electric shower with a mixer, and that the amount of grey water generated was 70 l. Therefore the energy required to raise the temperature of the preheated water to 40°C was estimated as:

$$Q = (4186J/kg°C)\times(70)kg\times(40°C - 25°C) = 4.4\times10^6\,J$$

$$4.4\times10^6\,J = \left(\frac{4.4\times10^6}{3.6\times10^6}\right)kWh = 1.22kWh \quad [4\text{-}43]$$

If the water was not preheated, the energy required to raise the temperature would be:

$$Q = (4186J/kg°C)\times(70)kg\times(40°C - 0°C) = 11.7\times10^6\,J$$

$$11.6\times10^6\,J = \left(\frac{11.6\times10^6}{3.6\times10^6}\right)kWh = 3.22kWh \quad [4\text{-}44]$$

This means the system should be able to reduce the energy cost from water heating by:

$$\% = \frac{3.22 - 1.22}{3.22} \times 100 = 62\% \quad [4\text{-}45]$$

Thus the amount saved from heat recovery is:

$$\left(\frac{£0.15}{kWh} \times 3.22kWh \right) \times 365 \times 0.62 = £109/yr \quad [4\text{-}46]$$

Hence the total cost savings from water and heat energy recycling equates to £198.42 per year, with a yearly operating cost of £24/yr. The fact that the yearly cost savings is higher than the operating cost suggests that the system could effectively save consumer money. For consumers without a water meter, a yearly cost saving of £109/yr can be realised from heat recovery alone. There are currently several grey water recycling technologies in the market, which can compete with the Arvia process, these technologies are discussed in Appendix G and their cost savings highlighted. Apart from the maintenance cost, replacement cost and the capital cost which have not been considered, there are several other factors such as the cost of electricity that can have an impact on both the operating costs and the cost savings, these factors are considered below.

4.7.5 Factors affecting cost benefits

4.7.5.1 Energy prices

The cost of electricity to consumers typically increases every year. It is likely that a change in the cost of electricity would affect the operating cost. According to Committee on Climate Change (2014) the cost of electricity is predicted to increase by 33% in the residential sector between 2009 and 2020, which equates to a rise of 2.9% per year. Taking this into consideration, the plot in Figure 4.71 expresses the effect of changing energy price on the operating cost and cost savings respectively over the next 5 years. The plot indicates that both the operating cost and cost savings increases proportionally with an increase in the cost of electricity. However, the increase in operating cost at £5 is much less than then increase in cost savings at around £20, due to the low operating energy required to operate the system. This therefore suggests that the cost savings can compensate for the operating cost if electricity price increase overtime. Although it has been suggested that the cost of electricity in the future is not expected to increase significantly due to investment in low carbon technology (Committee on Climate Change, 2014).

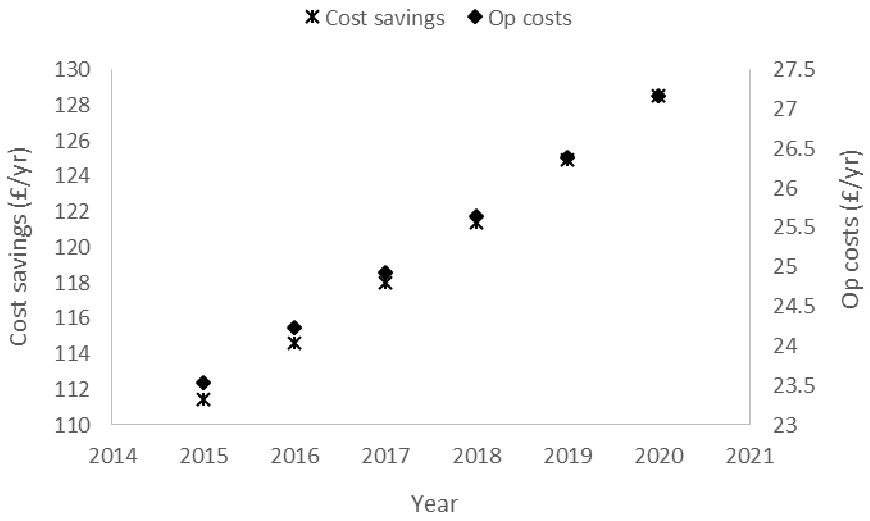


Figure 4.71 – Effect of yearly energy increase over the next 5 years on operating cost and savings

4.7.5.2 Grey water capacity

In the case of a household or if an individual spends longer in the shower, the volume of grey water generated increases. If the amount of organic load remained below 724 mg/l, which is likely for grey water sourced from the bathroom, the amount of energy required for electrochemical regeneration would not increase. This therefore means that an increase in the grey water capacity does not have a significant effect on the estimated operation cost, and is most likely to decrease in reality due to the lower organic load of the diluted grey water. On the other hand, an increase in the grey water capacity would result in an increase in the amount of grey water

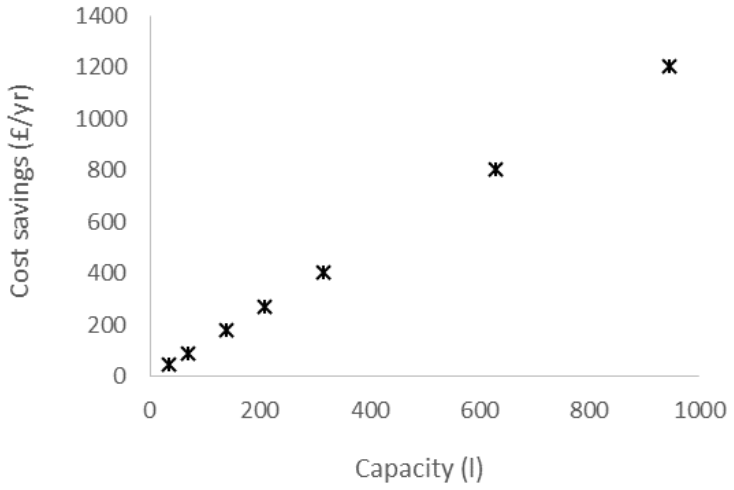


Figure 4.72 – Effect of grey water capacity on savings

The effect of increased grey water capacity on sewerage and water savings due to increased number of users/time spent in the shower is expressed in Figure 4.72. The plot indicates that a higher cost savings can be realised as the grey water capacity increases.

4.7.5.3 Efficiency of heat recovery

Changes in the heat recovery efficiency would affect the yearly savings, this effect is depicted in Figure 4.73. As expected the plot indicates that increasing the heat recovery efficiency results in an increase in the savings per year up to a maximum saving of around £190/yr. However according to the rules of thermodynamics, it is not possible to achieve heat recovery efficiency of 100%. Analysis of the heat recovery in section 4.6.3 showed that the maximum

percentage heat recovery is 75% which means a maximum possible cost savings of £135/yr from heat recovery

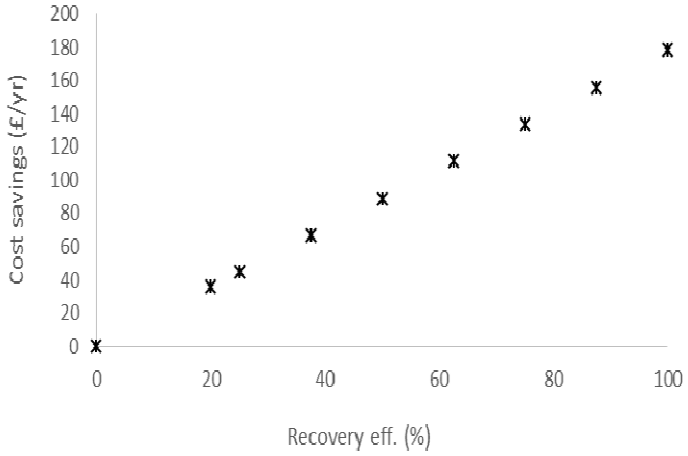


Figure 4.73 – Effect of heat recovery efficiency on savings

4.7.6 Summary

A cost benefit analysis was carried out to determine the total cost savings that could be obtained from using the technology with and without heat recovery. To determine the possible cost savings, the operating cost from pumping and electrochemical regeneration was estimated and subtracted from the estimated cost from water and energy recycling. The effect of carrying electricity cost, grey water capacity and heat recovery efficiency was also considered in the estimation. It was noted that because the operating cost was so low, varying the electricity cost and water capacity did not have a detrimental effect on the savings. However, other costs such as maintenance cost and the capital cost, which are not yet determined at this stage of the project hence were not considered could have significant effect on the savings. The estimated savings from heat recovery was fairly high that consumers without a water meter can also benefit from the technology. However, the cost savings from heat recovery is dependent on the heat recovery efficiency. Hence, it is important that the heat recovery system incorporated to the technology is able to achieve the highest heat recovery efficiency possible for the technology.

CHAPTER 5: CONCLUSIONS, RECOMMENDATIONS AND FURTHER WORK

5 CONCLUSIONS, RECOMMENDATIONS AND FURTHER WORK

5.1 Conclusions

Work carried out in this project has demonstrated for the first time the effectiveness of the removal and destruction of organic contaminants from a synthetic grey water, by continuous adsorption onto a graphite intercalation compound followed by its electrochemical regeneration. In addition, a 4-log reduction in microorganisms present in the grey water was observed during this continuous adsorption and electrochemical regeneration process. There was no evidence that the treatment process was able to remove inorganic contaminants from the synthetic grey water.

The process was evaluated in batch adsorption and electrochemical regeneration studies to understand the adsorption characteristics of Nyex™ adsorbent, as well as to determine if the adsorbent could be electrochemically regenerated when saturated with contaminants from the grey water. Continuous adsorption and electrochemical regeneration studies were conducted using the electrochemical cell to determine if continuous removal of contaminants could be achieved.

Batch adsorption study revealed that the initial uptake rate of organic contaminants by Nyex™ was very rapid (especially at high initial COD concentration (section 15.3.1)) with the majority of the active adsorption sites being occupied within minutes. This was to be expected due to the non-porous nature of the Nyex™ adsorbent. The adsorption kinetic data was analysed using a pseudo-second order adsorption kinetics model which predicts that the adsorption of organics onto Nyex™ is proportional to square of the initial concentration of the organics in the aqueous phase (concentration driving force). This prediction was confirmed by the high experimental adsorption rates of organic contaminants observed at higher initial COD concentration.

The experimental adsorption isotherm curve obtained demonstrates multi-layer adsorption of organic contaminants onto Nyex™ (based on COD value), with strong chemical adsorption

onto the surface of the Nyex™ and then subsequent layers formed by Van der Waals adsorption.

Only monolayer adsorption of anionic surfactant was observed, where it is postulated the hydrophobic tail adsorbs onto the Nyex™ and with the ionic hydrophilic head remaining in solution. This alignment of surfactant is supported by the observation of only monolayer adsorption as this configuration reduces the chances of multilayer formation, as the ionic hydrophilic head will have a greater affinity to water molecules in the grey water solution than to other adsorbed surfactant molecules. The monolayer arrangement of anionic surfactant meant that only 4% removal efficiency was observed compared to 20% treatment efficiency noted for COD. It was also observed that increasing the mass of Nyex™ led to an increase in the removal efficiency of anionic surfactant which probably indicates that the monolayer adsorption energy of the anionic surfactant at increased mass of Nyex™ is higher than the remainder of the COD.

One of the key findings from this work is that batch studies of the electrochemical regeneration process showed that the full adsorption capacity of the adsorbent can be recovered using a charge of 22 C/g of Nyex™. Complete regeneration of the adsorbent indicates that no organic by products generated are able to re-adsorb during the electrochemical regeneration process.

The adsorption and regeneration properties of Nyex™ were determined, the adsorbent was placed in the electrochemical cell and continuous adsorption studies were conducted to determine if the adsorbent can retain its adsorptive characteristics. However, results obtained from the continuous adsorption study demonstrated poor use of the packed adsorbent bed with breakthrough of organic contaminants occurring immediately. It was also noted that the flowrate and initial concentration had very little effect on the breakthrough curve. This was found to be attributed to the presence of flow channelling or bed spouting. The flow channelling through the bed resulted in poor distribution of grey water through the packed bed. The inefficient use of the packed adsorbent bed meant that the system was not able to achieve the required treatment consent for all operating parameters studies.

Results from the continuous adsorption and electrochemical regeneration study provided evidence that electrochemical regeneration of the packed bed of Nyex™ was being achieved. In the absence of electrochemical regeneration, whereby no electric current was applied across the cell, the treatment efficiency was 37% for COD. In contrast, when electric current was applied across the cell, at a current density of 16 mA/cm^2, a treatment efficiency of 63% and 25% was observed for COD and anionic surfactant respectively. However, operating the system at a higher current density resulted in an increase in the cell potential as well as a reduction in the current efficiency. The cell potential also doubled when no NaCl was present due to the low electrical conductivity of the NaCl free system.

Predicted breakthrough curve for different mass of Nyex™ using the Thomas adsorption dynamic model showed that increasing the mass of Nyex™ improved the breakthrough curve profile with a longer breakthrough time achieved when the mass of Nyex™ was over 30 kg. The increase in the Nyex™ mass appeared to supress the effect of flow channelling resulting in a breakthrough time of 1380 minutes. However, increasing the mass of Nyex™ would reduce the portability of the system as well as increase in the operating cost.

The mechanism of microorganism removal from grey water was investigated, and results suggested that the main method through which microorganisms were being removed was through electro-chlorination. A high removal of 4-log reduction in microorganisms was observed only when NaCl was present in the continuous adsorption and electrochemical regeneration system.

This level of organic and microorganism removal is a very positive starting point and suggests that there is significant potential for the system as a grey water and energy recycling unit. Whilst the system has several advantages over current grey water treatment technologies, significant work is required to further develop the unit into a viable technology that can satisfy both technical and commercial requirements.

As a next step in this project it is necessary that further development of the system is carried out in order to improve the treatment efficiency with lower operating cost. In the next chapter, various recommendations are provided of ways the system can be improved in order to overcome the difficulties highlighted in this thesis.

A brief investigation into the heat lost from the system was conducted. It was determined that due to the low heat lost experienced from the insulated system the grey water can be stored for around for around 20 minutes with little or no heat lost, negligible heat lost was also noted as the grey water travels through the pipe. This was achieved using insulation with thermal conductivity of 0.04 W/mK which comes in quite bulky. A thinner insulation material would be more expensive. Recovery of heat close to the bath/shower outlet was therefore considered to limit insulation requirement using a drainage pipe heat recovery unit. The calculation indicated that it may be possible to increase the mains temperature from 8°C to 30°C with a coil length of 3m which may not be possible. A more sensible increase to 20°C was proposed requiring a coil length of 1 m.

A cost benefit analysis of the unit indicates that a cost saving of £198/yr is possible. However, only the operation cost was considered in the analysis leaving out other possible costs such as maintenance which may result in a reduction in the estimated saving. The effect of residential electricity price rise and changes in the grey water capacity were also taken into consideration, but these were found not to be detrimental to the cost savings due to the low operating cost of the system.

5.2 Recommendations and Further Work

5.2.1 Process improvement

The main issue with the electrochemical cell used in this project was the occurrence of flow channelling within the adsorbent bed as well as the grey water short circuiting or bypassing the bed, which resulted in premature breakthrough time. The presence of flow channelling was resulted in poor distribution of the grey water by the nozzle installed at the bottom of the electrochemical cell. Hence, one way of improving the system is to improve the distribution of grey water throughout the bed to avoid premature breakthrough as well as to make use of the full adsorption capacity of the packed bed of Nyex™. Another possible factor requiring further development is the possibility of a NaCl free system. NaCl was added to the system as an electrolyte in order to increase electrical conductivity, but was not removed by the system and thus remained in the treated grey water. Hence it would be advantageous to further develop the

system so that it can operate without NaCl. Different methods have been considered for improving the system, one of which was improving the current upward flow system with NaCl catholyte in the cathode compartment. Another possible method considered was the use of a downwards flow system, which meant flow channelling is avoided and the system is able to make better use of the adsorption capacity of the bed. The third method considered was the use of a development Nyex™ which is 20 times more efficient in terms of adsorption capacity.

Upwards flow system (current configuration)

Predicted breakthrough curves generated using the Thomas adsorption dynamic model, indicated that increasing the mass of Nyex™ to 30 kg would result in an increase in the breakthrough time, with the time taken for 1% breakthrough increasing to around 1700 minutes (28 hours). This means that at a feed flowrate of 10 l/h (corresponding to a velocity of 1.78 m/h), the system should be able to treat 280 litres of grey water. However, increasing the mass of Nyex™ would mean an increase in the bed height to 6.25 m if the width and length of the bed were kept constant.

With a bed length of 6.25 metres, it would take 3.4 hours for the grey water to reach the top of the bed. A larger electrode area would also be required which would increase the operating cost of the unit. In addition, it may not be feasible to install a device 6.25 metres in length especially in residential buildings. It may however be possible to decrease the length of the bed by decreasing the treatment capacity from the 280 litres estimated earlier to the design capacity of 70 litres estimated in section 20.2. Decreasing the treatment capacity to 70 litres means the height of the bed can be reduced to 1.6 meters, which requires 8 kg of Nyex™. The minimum charge required to achieve 100% regeneration efficiency was estimated in batch mode as 22 C/g. Based on a Nyex™ mass of 8 kg and a current of 10 A, the time required for the system to achieve this charge was estimated as 5 hours. Increasing the current passed across the unit should reduce the treatment time. The cost for electrochemical regeneration of the Nyex™ was estimated as 8.6 kWh/m^3.

Another method for improving the adsorption profile is to carry out further work to develop the nozzle at the bottom of the cell so that the grey water can be better distributed around the

bed. Improving the distribution of grey water means the full capacity of the bed can be utilised, which means less Nyex™ is required for treatment. Using less Nyex™ would in turn reduce the amount of energy required for electrochemical regeneration as the treatment time required for electrochemical regeneration decreases.

Although it may be possible to improve the current configuration by increasing the mass of Nyex™ and/or improving the distribution nozzle, the system still requires the use of NaCl in the cathode compartment. When the system was operated without NaCl and with Nyex™ in the cathode compartment in place of the catholyte (non-catholyte system), the cell potential doubled and treatment efficiency decreased (section 16.2.3).

Arvia has conducted further development of the technology based on some of the results obtained from this work. Instead of developing the nozzle, a downward flow method was used in which the grey water is introduced from the top of the cell rather than the bottom. This treatment method was studied for the treatment of grey water and recommendation for design and further work are discussed in the next section.

Downwards flow system (Improved configuration)

Work conducted by Arvia Technology have shown that introducing the grey water at the top of the cell so that it flows downwards through the packed bed, enables better distribution of the wastewater around the bed. The weight of the influent solution flowing downwards also helps to compress the packed bed thus reducing resistance as the conducting Nyex™ is better able to act as a conducting bridge. This in turn improves the electrical conductivity of the system and reduces the cell potential, which means no NaCl is required. The unit was studied at various experimental conditions and results from the study were discussed in section 17.4. A total of 50 kg of Nyex™ was placed in the anode and cathode compartment of the cell, and based on previous studies, it was expected that complete removal should be achieved. However, the system was only able to achieve 56 % treatment efficient based on COD value. The adsorption kinetics as expected was fast with a rapid reduction in the organics concentration within the first few minutes after which a plateau was noted as the system approached equilibrium. The plateau observed could be attributed to two possible scenarios as discussed below.

Scenario 1

One possible cause of the plateau observed in the result could be as a result of organic products generated through electrochemical reduction of organics present in the cathode compartment. The generation of organic products in the cathode compartment of the system have recently been discovered by Arvia™ Technology. These organics can only be removed through electrochemical oxidation at the anode as the grey water is recycled continuously, and thus accumulates in the treated water over time. Further work is required to determine the rate at which these organic products are generated and removed from the system. Further work is also required to determine ways of preventing the generation of these organic breakdown products. One probable way to prevent formation of organic products is to only feed through the anode compartment, which means that as the flow of current is reversed, the flow of influent solution would be varied accordingly.

It is important that the Nyex™ in the anode compartment is completely regenerated before the flow of current is switched (anode changes to cathode compartment) to avoid formation of breakdown products in the cathode compartment.

Scenario 2

Another possible explanation could be due to the fact that the system reached equilibrium at this point where no further treatment was taking place. If this was the case, it would be beneficial to pass the grey water through a series of electrochemical cells. The COD of the grey water passed through the cell was reduced from 780 mg/l to 480 mg/l after the first cycle. A cycle is the time taken for the total volume of grey water of 250 l to pass through the electrochemical cell, and at a feed flowrate of 500 l/h, the time taken per cycle was 30 minutes. The amount of COD removed per cycle was estimated as 71250 mg COD, which means the grey water would need to be passed through 3 cells in series to reduce the organic contaminants down to the required consent level. The energy required for electrochemical regeneration for the downwards flow unit was 1.9 kWh/m^3, using 3 units would mean the energy requirement increase to 5.7 kWh/m3 which is much lower than the 8.6 kWh/m^3 estimated for the upwards

flow unit. This indicates that in the long run, the downwards flow unit would be more beneficial as a benchmark for future development.

Use of Development Nyex™

Extensive research have to date been conducted as a PhD project at Manchester University to further develop Nyex™. It has recently been reported that it may be possible to formulate an improved version of Nyex™ which has 20 times more adsorption capacity. Increasing the adsorption capacity of Nyex™ would have a significant effect on the operating and capital cost of the unit as the size of the system will be smaller with reduced electrode area. For instance, in the case of the downwards flow unit, using an adsorbent with 20 times more adsorption capacity would increase the mass of COD adsorbed from 71.25 grams to 1425 grams, thus reducing the mass of Nyex™ required per unit in series to 2.5 kg.

It would appear that the best possible configuration will be a downward flow unit which requires no NaCl and uses less energy for electrochemical regeneration. Feeding the grey water only through the anode compartment and feeding the grey water through a series of electrochemical cells could also increase the treatment efficiency. In addition, incorporating the development Nyex™ would significantly reduce the mass of Nyex™ required in the cell (due to increase in adsorption capacity) which in turn would result in further reduction in the operating cost.

5.2.2 Additional suggestion for further work

Breakdown products

During the electrochemical regeneration process, it is likely that electrochemical oxidation of Nyex™ loaded with organic contaminants from grey water results in the formation of breakdown products. Although extensive research have to date been undertaken to determine the breakdown products from electrochemical oxidation of Nyex™ loaded with Phenol (Hussain 2012), further work is required to understand the breakdown products generated during electrochemical oxidation of Nyex™ loaded with organics from grey water. In the case

of the non-catholyte unit, further work is also required to determine the breakdown products during electrochemical reduction of Nyex™ loaded with organics from grey water. Determining the breakdown products generated during electrochemical regeneration is very important to ensure safe reuse of the treated grey water for non-contact use.

Removal of suspended solids

Regulations for grey water reuse in the UK recommends that the treated grey water should be nearly free from suspended solids with the total suspended solids (TSS) content reduced to 30 mg/l. Although a detailed investigation on the removal of suspended solids was not conducted in this work, analysis of some of the treated grey water samples collected from the continuous adsorption process using the electrochemical cell indicated removal of suspended solid from the grey water. This could be due to suspended solids getting trapped between the packed bed of Nyex. Further work is however required to verify these results and to subsequently determine the mechanism by which suspended solids are removed. It would also be worthwhile to investigate other means through which to effectively remove suspended solids.

The main methods used by numerous researchers for the removal of suspended solids are through chemical and physical treatment methods such as coagulation (Bani-Melhem and Smith 2012; Pidou et al. 2008; Lin et al. 2005) and filtration (Al-Hamaiedeh and Bino 2010; March et al. 2004) respectively. Both methods can be beneficial, although further work is required if necessary to determine the most effective in terms of treatability and cost.

Electrochemical regeneration

The charge required to achieve 100% regeneration efficiency was determined in batch experimental mode as 22 C/g. However, in continuous mode, grey water is fed continuously into the cell which may have an effect on this regeneration efficiency. Result from this study showed that the cell was not fully regenerated when the system was operated in continuous adsorption and electrochemical regeneration mode. However, it was difficult to determine the optimum charge required due to flow channelling and the grey water by passing the bed. Hence it is necessary to define the optimum charge required to achieve 100% regeneration efficiency

in continuous mode. The reformatting of the cell from upward to downward flow may well help improve this efficiency.

Adsorption

Successful adsorption of organic contaminants was observed, although adsorption of anionic surfactants was limited and inorganics were not adsorbed, due to their lower affinity to the surface of Nyex™ compared to organic molecules. It may be possible to modify the Nyex™ surface in order to increase the adsorption capacity for anionic surfactants and to enable adsorption of inorganic molecules. Modification of carbon adsorbent to improve selectivity and adsorption capacity is an area that has previously been researched (Huang et al. 2009; Harry et al. 2007).

It is clear that there are a range of possible methods through which the GIC adsorption and electrochemical regeneration process can be developed. Carrying out further developments of the unit could potentially enable a viable design which could position this system above other available grey water recycling technologies.

Appendices

APPENDIX A

Synthetic Grey Water Formulation

Due to significant batch variability experienced with real grey water, it was concluded that synthetic grey water would be used as the adsorbate in order to effectively manage the experimental process. Using synthetic grey water would also enable repeatability and efficient control and adjustment of parameters. Bathroom grey water was used as the main source in this project and the synthetic grey water was formulated using guidelines provided by the British Standards Institution (BSI) for bathroom grey water. The BSI recommended using 86 ml of liquid soap, 97.5 l of de-chlorinated mains water and 1 ml of sunflower oil to make up 100 litres of synthetic grey water. However, the mains water used in this project was not de-chlorinated. The guideline also recommended using sewerage sludge to provide the required E.coli concentration of $10^5 – 10^6$ cfu/100 ml.

The sewerage sludge used for formulating the synthetic grey water was collected from settled sewage effluent from a secondary treatment process. The sewage effluent was then analysed at United Utilities laboratory to provide the required levels of coliforms. To formulate the synthetic grey water used in this project, 0.86 g/l Sanex zero shower gel was used as the liquid soap and was mixed with 0.01 g/l Tesco pure sunflower oil. The composition of the resulting synthetic grey water is detailed in Table A. 1. The composition of the synthetic grey water used in this project falls within the range given in the BSI guideline, apart from the COD value which was only very slightly higher that the range recommended in the BSI guidelines. The synthetic grey water was either diluted or concentrated to obtain the required concentrations.

Table A.1 - Synthetic grey water composition obtained using 0.86 g/l Sanex shower gel, 0.01 g/l Tesco Pure sunflower oil and sewerage sludge

Parameters	Unit	Value
pH		7.03 ± 0.5
COD	mg/l	249 ± 35
Anionic surfactant	mg/l	20 ± 5
TSS	mg/l	31 ± 10
Turbidity	NTU	40 ± 10
Chlorine	mg/l	1 ± 0.5
Nitrate	mg/l	0.2 ± 0.05
Nitrite	mg/l	0.05 ± 0.01
Ammonia	mg/l	0.02 ± 0.01
Phosphorous	mg/l	0.5 ± 0.1
E.coli	cfu/100 ml	$10^4 \pm 10^5$
Pseudomonas	cfu/100 ml	$10^4 \pm 10^5$

APPENDIX B

Current Efficiency Calculation Based on COD

The derivation of current efficiency discussed in this section of the appendix was taken from publication by Brown (2005) and is in agreement with the current efficiency reported by Comninellis and Pulgarin (1991) using the COD method.

The current efficiency was estimated as a ratio between the theoretical charge required and the actual charge used during operation. The theoretical charge required was derived based on the assumption that:

1 g of COD removed requires 1 g of oxygen = 0.0625 moles of oxygen atoms

The amount of COD removed can be estimated using the equation:

COD removed $= (C_0 - C)\, V$

Where C_0 = Initial COD concentration (g/l)

C = Final COD concentration (g/l)

V = Volume treated or passed through the cell (l)

Hence, moles of oxygen atoms required to remove COD = $0.0625\, (C_0 - C)\, V$

Assuming that during electrochemical oxidation, two electrons is required per oxygen atom involved in oxidation, which means the moles of electrons involved in the removal of COD can be expressed as:

Moles of electrons involved in COD removal = $0.125\, (C_0 - C)\, V$

The theoretical charge required in coulombs can be estimated as the product of the moles of electrons involved in COD removal and the Faraday constant (F) as follows:

Theoretical charge used = Moles of electrons required$*F$

Where F = Faraday constant (96,487 C mol^{-1})

Actual charge used $= It$

Where I = cell current (A)

t = treatment time (s)

Current Efficiency, CE = Theoretical coulombs required / Actual coulombs used

Hence the CE was calculation using the equation:

$$\text{Current efficiency, CE} = \frac{(C_0 - C)VF}{8It}$$

APPENDIX C

Adsorption Isotherm Data

Table C.1 - Adsorption isotherm data for COD removal, obtained from adsorption isotherm study carried out over a contact time of 1 hour with 7 g/l adsorbent and 150 ml synthetic grey water solution. Where C_0 and C_e are the initial and equilibrium liquid phase concentration, and q_e is the adsorbed phase concentration at equilibrium

Sample ID	C_0 (mg/l)	C_e (mg/l)	q_e (mg/g)
1	1278	1016	39.3
2	1160	900	39
3	1138	880	38.7
4	1068	816	37.8
5	884	680	30.6
6	711.9	573	20.91
7	605.1	470	20.34
8	514.3	380	20.23
9	437.2	320	17.65
10	371.6	280	13.82
11	315.9	245	10.71
12	268.5	210	8.85
13	228.2	175	8.06
14	194.0	145	7.42
15	164.9	120	6.81
16	148.4	105	6.58
17	133.6	91	6.46
18	120.2	83	5.66
19	108.2	70	5.80
20	97.4	62	5.38
21	87.6	58	4.52
22	78.9	53	3.95
23	71.0	47	3.67
24	63.3	49	2.14
25	46.3	38	1.25
26	33.9	30	0.59
27	5.7	3	0.40
28	0	0	0

Table C.2 - Adsorption isotherm data for anionic surfactant, obtained from adsorption isotherm study carried out over a contact time of 1 hour with 16 g/l adsorbent and 150 ml synthetic grey water solution. Where C_0 and C_e are the initial and equilibrium liquid phase concentration, and q_e is the adsorbed phase concentration at equilibrium

Sample ID	C_0 (mg/l)	C_e (mg/l)	q_e (mg/g)
1	56.84	48.8628	0.23932
2	50.96	42.9828	0.23932
3	43.316	35.1428	0.2452
4	36.064	29.2628	0.20404
5	32.928	24.7548	0.2452
6	17.836	10.9368	0.20698
7	12.544	8.0164	0.13583
8	6.9776	4.2336	0.08232
9	3.5672	1.9796	0.04763

APPENDIX D

Linearised Plot of the Adsorption Dynamic Model

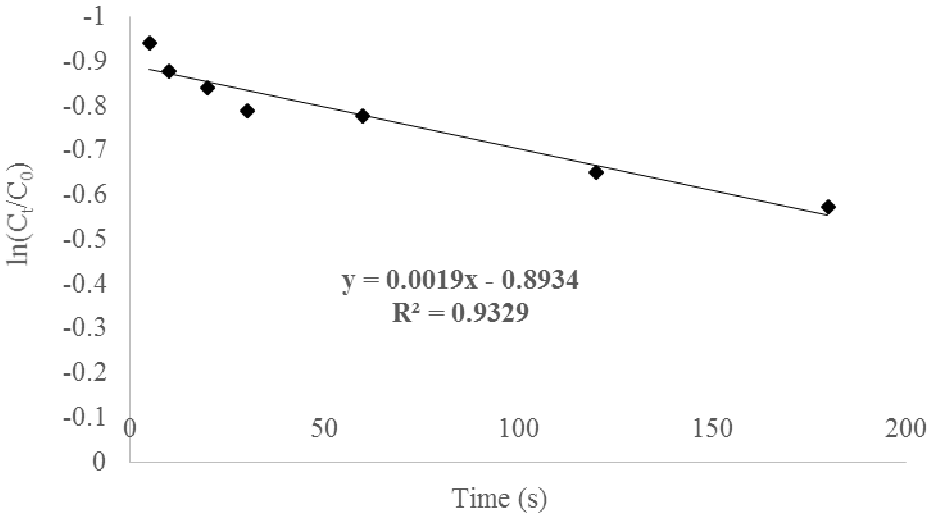


Figure D.1 - Adam-Bohart model; data obtained from studies conducted with initial influent COD concentration of 724±50 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm^2

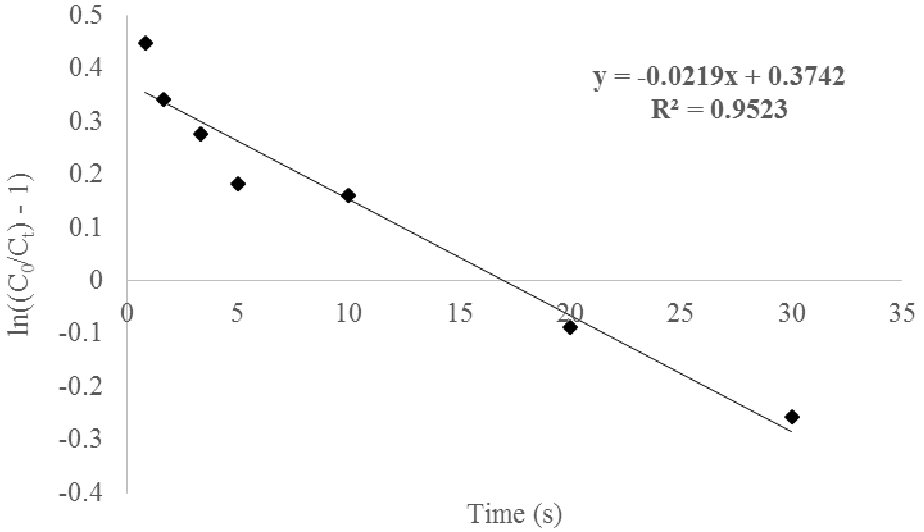


Figure D.2 - Thomas model; data obtained from studies conducted with initial influent COD concentration of 724±50 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm^2

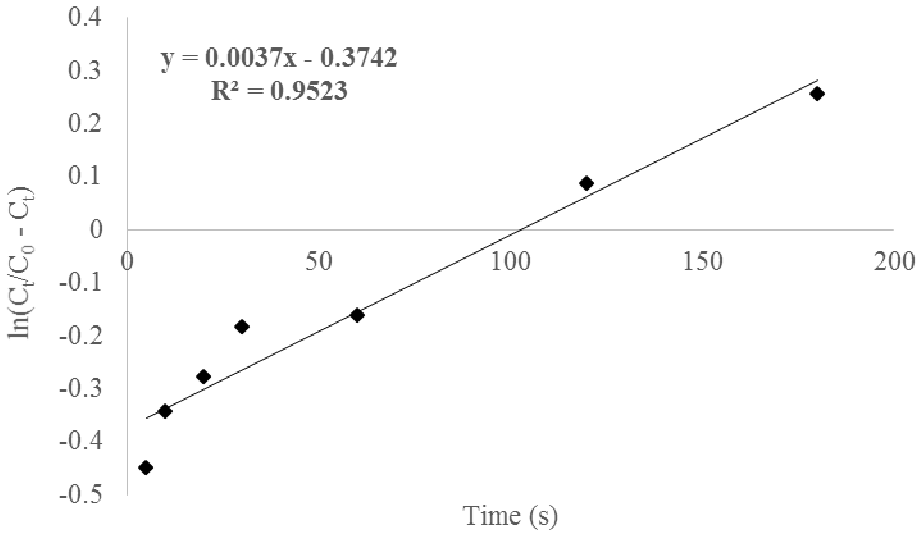


Figure D.3 - Yoon-Nelson model; data obtained from studies conducted with initial influent COD concentration of 724±50 mg/l, feed flowrate of 10 l/h and current density of 14.4 mA/cm^2

APPENDIX E

Heat Transfer Equation used for Heat Recovery Coil Design

The heat recovery calculation derived by Patil et al. (1982) was used to estimate the overall heat transfer coefficient use to design the drainage pipe heat recovery unit. The procedure was selected as it does not require the outlet temperatures as input variables in the calculation, which was an unknown variable. The procedure used to determine the overall heat transfer coefficient is detailed below.

Estimation of the overall heat transfer coefficient

The geometry of the coil was initially determined as follows:

Length of coil L, required to make N turns:

$$L = N\sqrt{(2\pi r)^2 + \delta^2}$$

$\infty = 1.5d_o$

Where ∞ is the pitch, which is the spacing between consecutive coil turns, r_{Av} is the average radius of the coil and d_o is the outside diameter of coil.

The equation for the volume available for fluid flow V_f, was derived using equation:

$V_f = V_a - V_c$

Va is the volume of the annulus = $(\pi/4)(C^2 - B^2)\infty N$

Vc is the volume occupied by the coil = $(\pi/4)d_o^2 L$

Where C is the inside diameter of the outer container and B is the outside diameter of the inner cylinder.

The shell side equivalent diameter of the coil D_e was estimated as:

$D_e = 4V_f/\pi d_o L$

The heat transfer coefficient outside (h_o) and inside (h_i) the coil were then determined using conventional methods for straight pipe. The inside heat transfer coefficient was corrected for coiled pipe by multiplying by $(1 + 3.5(D/D_H))$. Where D is the inside diameter of the coil and D_H is the average diameter of the helix.

The overall heat transfer coefficient U, is given by:

$$\frac{1}{U} = \frac{1}{h_o} + \frac{1}{h_i} + \frac{x}{k_c} + R_t + R_a$$

Where x the thickness of the coil, k_c is the thermal conductivity of the coil, R_i and R_o are the internal and external fouling factor respectively.

Estimation of the coil dimensions

The area A, required for heat transfer is determined by:

$A = Q/UA\Delta T_m$

Where Q is the heat load and ΔT_m is the log mean temperature.

Since $A = \pi d_o L$ and L can be expressed in terms of N, the number of turns of coil needed can be calculated by:

$N = A/(\pi d_o(L/N))$

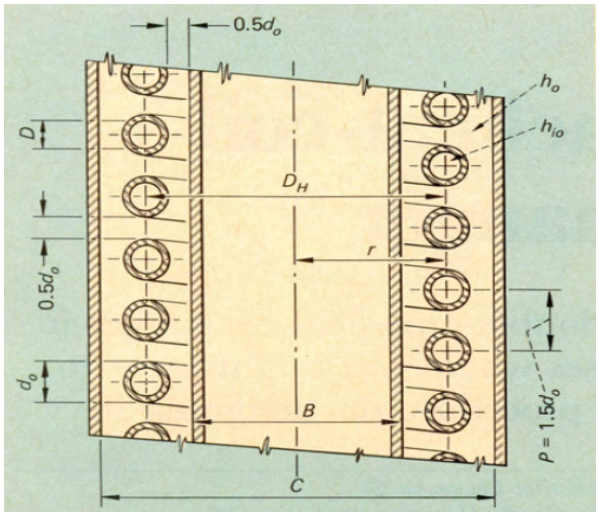


Figure E.1 - Schematic cutaway side view of the heat exchanger coil

APPENDIX F

Grey Water Treatment Processes

Grey water treatment systems vary from a very simple and cheap diversion system with no treatment to a more complex and expensive system with a more intensive treatment. Any grey water system that requires storage of the grey water must incorporate some level of treatment as the condition of untreated grey water tends to rapidly deteriorate in storage. This rapid deterioration is due to the often warm, nutrient rich condition and the high organic content, which provides an ideal condition for bacteria to grow.

Since the 1970s, researchers have investigated methods of treating grey water. The technologies that were reported during this period were mainly physical treatment such as filtration, often coupled with some form of disinfection (Arika et al. 1966; Hall et al. 1974; Hypes et al. 1975; Winneberger 1974). Grey water treatment technologies seem to have become more advanced from the 1980s as by this time, researchers were investigating use of biological technologies such as bioreactors and membrane bio-filters (Brewer et al. 2001; Laine 2001; Santala et al. 1998; Surendran and Wheatley 1998).

Grey water treatment systems are often classified by the type of treatment, and this classification is used to group the various treatment systems that have been investigated. The type of treatments which have been studied are; *physical* (coarse and sand filtration, adsorption and membrane), *chemical* (photo-catalysis, coagulation, adsorption and electro-coagulation) and *biological* (rotating biological contactor, constructed wetland, membrane bioreactor).

Physical Treatment

There have been many reporting on the use of physical process for the treatment of grey water. These processes consist of mainly filtration which ranges from a simple sand filtration to a more complex and advanced membrane filtration process.

Sand filters use coarse or fine sands and at times other granular media to remove contaminants from water; whilst coarse filters use some form of strainer, foam or mesh. The difference between a coarse and sand filter is that the resident time for coarse filtration is shorter and it can only remove larger particles such as lint and hair.

Sand filters on the other hand are especially good for removing solid particles, and some levels of organic matter, bacteria and at times viruses.

The main advantages of the sand and coarse filtration is that they are cheap and simple. Although they are effective in removing turbidity, they have limited effect in removing other contaminants in grey water when used alone. For instance results obtained by March et al. (2004) using nylon sock type filters proved that use of coarse filter alone has limited effect in removing contaminants from grey water. The nylon filter, which was followed by a sedimentation and disinfection step (hypochlorite), was still only able to reduce the COD, total nitrogen, turbidity and suspended solids from 171 mg/l, 11.4 mg/l, 20 NTU and 44 mg/l to 78 mg/l, 7.1 mg/l, 16.5 NTU and 18.6 mg/l respectively. That is a reduction of 54%, 38%, 18% and 58% for COD, total nitrogen, turbidity and suspended solids respectively. On the other hand, study performed by Mandal et al. (2011) using a combination of coarse sand filter with a disinfection stage (the type of disinfection was not stated in report) achieved 60% turbidity reduction from an initial concentration of 20.6 NTU. There was also a 51% and 95% reduction in COD and total coliform from an initial concentration of 284 mg/l and 37400 cfu /100 ml.

In a study by Al–Wabel (2011) the treatment of grey water generated from hand and mouth wash (ablution) was evaluated using a combination of four sand filters, one activated charcoal filter and a UV steriliser. Using the sand filter alone, the COD and turbidity was only reduced from 500 mg/l and 0.95 NTU to 480 mg/l and 0.47 NTU respectively. Incorporating the activated carbon filter and UV disinfection helped to reduce the COD and turbidity further down to 340 mg/l and 0.12 NTU. This shows that, like coarse filters, sand filters also cannot be used alone. Ushijima et al. (2012) investigated the performance of the slanted soil treatment process using several different chambers containing coarse and fine soil. The result showed that the fine soil presented a much better removal of suspended solids, pathogen and total COD compared to the coarse sand which did not retain most of the pathogens. Itayama et al. (2006) also performed a study using slanted soil filter utilising only coarse sand media.

The slanted soil filter used in Itayama et al. (2006) study was only able to retain 78% of suspended solid contaminants compared to the 97% removal achieved in the study by Ushijima et al. (2012). However, using fine sand blocked the system within a short time period thus

increasing the maintenance requirement. Ushijima et al. (2012) suggested that combining the fine and coarse sand would extend the time before blockage.

The main advantages of the sand and coarse filtration is that they are cheap and simple. Although they are effective in removing turbidity, they have limited effect in removing other contaminants, such as dissolved contaminants. Adding other treatment processes however can make the system more operationally complex and expensive. Al–Wabel (2011), Itayama et al. (2006), March et al. (2004) and Ushijima et al. (2012) claimed that their treated grey water can be used for toilet flushing and in some cases for restricted irrigation. However, using the reclaimed grey water just for toilet flushing or gardening does not provide enough economic benefits as illustrated by the 14 years payback period put forward by March et al. (2004).

Membrane filtration systems offer a permanent barrier for very small particles and molecular compounds. The treated water is thus extremely low in turbidity and coliforms. In 1998, Birks investigated the use of ultrafiltration (UF) to treat grey water with medium contaminant load (451 mg/l COD), and the system was able to achieve 74% reduction in COD. Li et al. (2007) also studied the effectiveness of a system which uses a submerged spiral wound ultrafiltration membrane module. The study showed that the system was able to reduce total organic compound (TOC) by 82% and turbidity by almost 100%. Since the pore size of these UF membranes are 0.1 microns, the water will be completely free of pathogens. However, UF was unable to remove dissolved nutrient and organics.

Ramona et al. (2004) investigated the potential of membrane filtration using UF and nanofiltration (NF) on light grey water (low contaminant load; 170.3 mg/l COD, 29.8 mg/l suspended solids). At the lowest molecular weight cut off (MWCO) of 30 kDa, the ultrafiltration (UF) system obtained a COD and turbidity removal efficiency of 69.3% and 96.6% efficiency respectively, though BOD removal was not very effective.

The reclaimed water produced by the nanofiltration (0.2 kDa) system was of higher quality with 93.3% removal efficiency of COD. Ramon et al. (2004) claimed the treated water from the nanofiltration system is suitable for unrestricted reuse due to the high removal of organic matter and partial removal of ionic species. Šostar-Turk et al. (2005) was also able to achieve 98% COD removal efficiency using UF and reverse osmosis (RO) membrane. Although the RO and the NF systems seem to be very effective in removing contaminants, the high energy

required to overcome the pressure within a RO and a NF system makes them less cost effective to operate.

One thing to keep in mind is that with membrane filtration, the level of the influent contaminant load is paramount to its efficiency. Increase in particulate matter concentration in the influent results in shorter blockage and fouling time. This increases the hydraulic resistance of the membrane, and as a result, increasing the energy demand. The physical system reported by Ward (2000) was one of the physical systems using a combination of sand and membrane filter, and was able to achieve unrestricted reuse standards, but the initial concentration was extremely low. According to Kim et al. (2009), the microfiltration process is more economical when compared to other membrane filters. However, since it only removes turbidity, suspended solids and some levels of COD, permeate from the micro-filter will have to go through another treatment or disinfection stage to remove biological and dissolved organics. This means that filtration in itself is not sufficient to guarantee adequate removal of organic contaminant to prevent re-growth of biological organisms.

Chemical Treatment

Limited chemical treatment processes have so far been reported for grey water treatment. The chemical treatment processes that have been reported to date are coagulation, ion exchange adsorption on granular or powdered activated carbon and photo-catalytic oxidation.

The coagulation process is especially effective in removing solid particles from grey water. In a study by Pidou et al. (2008) using coagulation with aluminium salt coagulant, the COD and turbidity were reduced after treatment to 287 mg/l and 4.28 NTU, corresponding to a removal of 63% and 91% respectively.

Based on the quality of the treated grey water achieved in the study by Pidou et al. (2008), it can be seen that although removal of suspended solid is effective, the coagulation process alone is not enough to reduce organic substances to the required discharge or reuse standard of below 100 mg/l COD concentration (Lin et al. 2005; Šostar-Turk et al. 2005). Šostar-Turk et al. (2005) performed a study using a treatment method of coagulation and then adsorption on granular activated carbon (GAC) to treat laundry wastewater. Using coagulation alone and with aluminium salt coagulant, the COD concentration was reduced from 280 mg/l to 180 mg/l whilst the BOD and suspended solid concentrations were reduced from 195 mg/l and 35 mg/l

to 100 mg/l and less than 5 mg/l respectively. That is a removal of only 36% and 51% for the COD and BOD respectively compared to the 93% and 95% reduction noted when GAC treatment process was integrated to the coagulation process.

Lin et al. (2005) reported a treatment method consisting of a combination of electro-coagulation followed by a disinfection step using sodium hypochlorite. Results from the study showed a COD, BOD and turbidity reduction from 55 mg/l, 23 mg/l and 43 NTU to 22 mg/l, 9 mg/l and 4 NTU respectively. The treated grey water quality meets the water reuse standard proposed in the study. However, the contaminant concentration in the influent grey water was very low, making it difficult to come to a real conclusion on the effectiveness of this treatment process.

The magnetic ion exchange resin process used in a study performed by Pidou et al. (2008) was able to reduce the total coliform in the influent grey water to 59 /100 ml which meets the reuse requirement for restricted usage. However the COD, BOD and turbidity were only reduced from 791 mg/l, 205 mg/l and 46.6 NTU to 272 mg/l, 33 mg and 8.14 NTU. This shows that the magnetic ion exchange resin process alone also failed to reduce the BOD and the turbidity concentrations to the required reuse standard of 30 mg/l and less than 5 NTU respectively.

Photo-catalytic oxidation (mainly using titanium dioxide) is a fairly new treatment process and according to a study by Sanchez et al. (2010) has proved to be effective in removing dissolved organics and anionic surfactants particularly in light grey water. Based on the treatment level obtained from this study, it was concluded that this treatment process will also need to be integrated with other technologies, as photo-catalytic oxidation alone will not provide efficient treatment of grey water with dissolved organic concentration above 100 mg/l. Another issue likely to arise from using the photo-catalytic oxidation is keeping the titanium dioxide photo-catalyst on the surface of the water (higher density than water, thus sinks in water), in order to enable optimum oxidation.

Biological Treatment

Biological processes currently available for processing grey water are constructed wetlands, up-flow anaerobic sludge blanket (UASB), sequencing batch reactor (SBR), rotating biological contactor (RBC), and membrane bioreactor (MBR). Aerobic biological treatment processes are very effective in breaking down organic waste. As a result, aerobic treatment usually yields

better effluent quality than the anaerobic treatment process within a short retention period. Hernández Leal et al. (2010) performed a study which compares the SBR (aerobic biological treatment), UASB (anaerobic biological treatment) using grey water with COD concentration of over 827 mg/l and was successful in achieving 90% COD removal. The study showed that the aerobic SBR system is more effective in treating grey water achieving the maximum COD removal of 90% compared to 51% achieved using the anaerobic UASB system. This was thought to have been due to poor removal of suspended fraction of the COD in the anaerobic system. Lamine et al. (2007) also achieved 90% COD removal efficiency using an SBR system to treat grey water with lower influent concentration of 102 mg/l.

The RBC consists of a rotating disk which carries a bio-film where organic contaminants are adsorbed from the grey water. Like the SBR, the RBC process is also aerobic; air is bubbled to transfer oxygen into the grey water. In literature, the RBC, like many other biological systems are rarely used individually, but are rather at times preceded by some form of physical pre-treatment and are followed by a filtration and or disinfection step. For instance, in a study by Friedler et al. (2005) an RBC system was used to treat a low strength influent concentration of 158 mg/l COD. The system was preceded with a coarse filtration step followed by a sedimentation step used to remove lint, hair and sludge from the grey water. A sand filtration and then chlorination step followed the RBC system. The study showed that the level of COD, turbidity (influent 33 NTU) and faecal coliforms (influent $5.6x10^5$ /100 ml) was reduced by 71%, 94% and 98% respectively, with a further reduction of 75%, 98% and over 99% respectively after the sand filtration and chlorination step.

Similarly, Eriksson et al. (2009) reported use of an RBC system, which was preceded with a settling tank followed by 3 RBC systems in series, another settling tank, a sand filter and then a UV treatment process. The system achieved 82% reduction in COD in the final effluent, from an initial concentration of 142 mg/l.

MBR is a suspended growth activated sludge system that utilises a combination of aerobic biological treatment and filtration to encourage both consumption of organics and filtration of pathogens and solids. The process is highly effective, if designed and utilised properly. It is also the only biological treatment system that does not require a filtration or disinfection step following treatment. Compared to all other biological processes, the MBR has a high degree

of operation flexibility as it can accommodate influent grey water of varying qualities and quantities. Liu et al. (2005) reported use of a submerged MBR to treat bathroom grey water; using eight hollow fibre membrane modules. The effluent from the system was clear, free from suspended solids, and the faecal coliform was not detectable. The study also demonstrated a 91% COD reduction from an initial average concentration of 211 mg/l. Lesjean and Gnirss (2006) also reported effective treatment using a submerged plate and frame MBR to treat grey water sourced from the kitchen. The system was able to reduce suspended solid concentrations to below 1 mg/l, the COD concentration was reduced to 24 mg/l in the effluent, corresponding to a reduction of 95%. The primary disadvantage of utilising an MBR is the high capital and operating costs in comparison to other treatment process with similar throughput. The type of membrane used for the MBR (MF, UF, NF or RO) was not stated in both reports. This is very important as membranes such as RO and NF although would provide higher quality reclaimed water, may not be economically viable due to the high energy requirement and their short fouling time.

Constructed wetlands have in the past been successfully used to treat wastewater and are considered as an environmentally friendly approach. The process utilises a combination of physical, chemical and biological processes. The filtration step occurs within the reed-bed upon which microorganisms grow. The microorganism and natural chemical process are responsible for the majority of contaminant removal. Gross et al. (2007) applied a recycled vertical flow constructed wetland for the treatment of mixed grey water. The suspended solids, faecal coliforms and COD were reduced to 3 mg/l, $2x10^5$ /100 ml and 157 mg/l, corresponding to reduction of 98%, 99.6% and 81% respectively.

The constructed wetlands are typically inexpensive and are very effective in removing contaminants (if properly designed). Some of the disadvantages of constructed wetlands are the large space requirement and the fact that surface water can attract mosquitoes and other pests.

Disinfection of grey water

Detection of microorganisms in grey water means that disinfection may be necessary to control potential health risk and to ensure compliance with microbial standards. Disinfection of Grey water can be achieved through different methods such as chlorination (Benami et al. 2015;

March and Gual 2009; Friedler et al. 2008; Winward et al. 2008a; Gual et al. 2008) and ultraviolet (UV) radiation (Benami et al. 2015; Couto et al. 2014; Friedler and Gilboa 2010; Gilboa and Friedler 2008). Chlorine disinfection is often used for grey water disinfection due to its effectiveness in removing almost all types of microorganisms, its widespread use for potable and wastewater disinfection as well as low cost. UV irradiation on the other hand, is a more advanced disinfection method which is gaining more attention for grey water disinfection due to its numerous advantages over chlorination. The advantages of the UV disinfection method is that compared to chlorination, it does not require storage for the disinfectant which could be hazardous, it is not thought to generate unwanted by-products and it does not require any dosing equipment (March and Gual 2009; Boorman et al. 1999). In addition, UV irradiation is more effective than chlorination in disinfecting a wider range of microorganisms (Metcalf 2003). However, UV irradiation is an energy intensive technique and does not provide any residual disinfection which protects the treated water from recontamination over a period of time, thus a secondary disinfectant is required (Friedler and Gilboa 2010).

Other disinfection techniques used to disinfect grey water are photocatalysis using titanim dioxide (Gulyas et al. 2009), disinfection using essential oil (Winward et al. 2008b) and hydrogen peroxide (Ronen et al. 2010). However, these methods generate disinfectant residual in the treated grey water, which would need to be removed. Electrochemical disinfection is considered to be a promising disinfection technique which has gained increasing popularity for water and wastewater disinfection but much less attention have been paid to its use for grey water disinfection.

Electrochemical disinfection is a promising alternative to chlorination as it requires no storage for the disinfectant and requires no dosing equipment. In addition, electrochemical disinfection technique provides residual disinfection which means it has advantages over UV irradiation.

Comparison of the Arvia™ process with other available treatment processes

The major contaminants that need to be removed in reclaimed grey water are organics, micro-organisms, nutrients and suspended solids. Based on the literature review of physical treatment processes, it is obvious that coarse and sand filtrations alone are not able to provide efficient removal of suspended solids, organics and microorganisms. Microfiltration and ultrafiltration are excellent at removing turbidity and pathogens, but are limited in their ability to remove

dissolved contaminants which may encourage re-growth of micro-organisms. The nanofiltration and reverse osmoses processes are effective in removing both dissolved and suspended organic contaminant, with almost 100% COD removal. However, these more advanced processes are fundamentally expensive and difficult to operate due to membrane fouling (especially when the contaminant load is fairly high). The Arvia™ process on the other hand can handle comparatively high contaminant load and is effective in removing dissolved organics. It also has the potential of disinfecting the final effluent due to the production of chlorine and chlorinate species through electrochemical reaction.

Compared to physical treatment processes, chemical processes are more successful in reducing levels of organic contaminants as well as turbidity from grey water, although contaminants are not reduced sufficiently especially for heavily contaminated grey water. The adsorption processes using activated carbon are widely used in WwTP. The activated carbon adsorption process is very similar in operation to the Arvia™ process, in that they are both adsorption of contaminants on graphite. The graphite adsorption processes are simple to operate and are particularly good at adsorbing organic contaminants and to some extent, inorganic contaminants. Šostar-Turk et al. (2005) demonstrated this from results obtained from a study using a combined system of coagulation and activated carbon adsorption.

The study showed that the COD and BOD removal was increased from 36% and 51% respectively using the coagulation processes to 93% and 95% respectively after activated carbon was used. The major drawback of utilising the activated carbon adsorption process is that once all the adsorption sites are filled, the activated carbon cannot be efficiently regenerated in a continuous process. However, the Nyex™ used in the Arvia™ process will not experience this issue as it is continuously regenerated through electrochemical regeneration. Another advantage of using Nyex™ over activated carbon and sand filters is the build-up of sludge and organic film over time. This build up is not generated in the Arvia™ process due to the high conductivity of the Nyex™, which enables quick and effective regeneration.

Literature review on biological treatment processes shows that, when compared to the anaerobic treatment processes, the effluent from an aerobic type biological treatment processes is more likely to successfully meet standards from unrestricted water reuse. This is due to the fact that the aerobic type treatment processes are able to remove biodegradable organic

contaminants within a short retention time, which means re-growth of micro-organisms is avoided. The aerobic type biological treatment processes include MBR, constructed wetlands, RBC and SBR. The biological system can effectively treat medium to heavily contaminated grey water. However, apart from the MBR process, a filtration and/or disinfection step is often required after biological treatment as poor removal of microorganisms and suspended solids has been reported when these systems are used alone. The MBR is the only technology that is able to achieve high effluent quality, but the MBR processes are more cost effective when used on a large scale (over 160 flats) (Friedler and Hadari, 2006, Lazarova et al., 2003).

The main advantage of the Arvia™ process over all other available processes is there is no sludge production. The Arvia™ process is able to adsorb and then destroy contaminants without any waste products. The Arvia™ process also produces chlorine through electrochemical oxidation reaction, which provides treatment for biological contaminants. If this project is successful, it will provide a very important development in the future of grey water recycling.

APPENDIX G

Existing Grey Water Recycling Technologies (Market Research)

There are currently several manufactures of grey water recycling system around the world, a brief overview of several systems has been carried out in order to get a general idea of what is already in the market.

Hansgrohe - Pontos HeatCycle & Pontos AquaCycle

The Pontos AquaCycle system recycles water from shower and bath for flushing the toilets, cleaning, washing clothes and watering gardens. The grey water is initially filtered to remove any coarse particles (e.g. hair and lint), the pre-filter is automatically backwashed and any residues flow into the drainage system. The filtered water is then fed into a two-staged aerobic biological treatment system where aerated micro-organisms remove water contaminants. Sludge generated during the biological treatment stage is drained off into the drainage system at an automated fixed regular interval. The water then flows through a UV lamp for disinfection, and is stored in the process tank ready for use. Hansgrohe claims the quality of the treated water conforms to the hygienic requirement of the EU Bathing Water Directive, and can be used for any application not requiring water of potable standards (Hansgrohe, 2012).

In early 2011, Hansgrohe developed the Pontos HeatCycle to incorporate both domestic wastewater recycling and heat recovery. The system has been developed to recover the heat from grey water sourced from bath and shower. The device is a heat exchanger module which is available as an add-on to the Pontos AquaCycle unit. Heat recovered in this way is in the order of approximately 10-15 kWh/m^3 of grey water, the energy is used to heat fresh water. The device is said to be even more efficient when combined with rainwater utilisation, as it can then be toped up with rainwater instead of potable water (Hansgrohe, 2010).

Hansgrohe claims the Pontos HeatCycle system can reduce the energy cost for hot water preparation by 20%, reduce water consumption as well as the amount of wastewater to treatment works by up to 50%, works purely biomechanically without any chemical additives and guarantees a short payback period (Hansgrohe, 2010). The system requires an operating energy of 1.2 kWh per cubic meter of grey water, and the length of the payback period is

dependent on the size of the system which has a capacity of up to 30,000 litres per day and is equivalent to about 50 households in the UK.

The AquaCycle 900 consists of three tanks, each of 300 litres capacity, and is ideally suited for residential buildings; larger models are available for apartment blocks, leisure centres, hotels, etc. The device costs £3750 (without installation cost) and uses 0.6 kWh of electricity to operate (Planet Energy Solutions, 2011). For a family home of up to four people, the total amount of water generated per day from bathroom usage is 450 litres/household/day. Assuming that 60% of the grey water generated is used for non-potable use, and with a water and sewerage charge of approximately £1.20/m^3 and £2.30/m^3 respectively (South West Water, 2015), the payback period of the AquaCycle 900 was calculated as follows;

$$\text{Water saving} - \left(\left(\frac{450\times365}{1000}\right)m^3\times0.6\right)\times£1.20/m^3 = £118.26/yr$$

$$\text{Sewerage saving} - \left(\left(\frac{450\times365}{1000}\right)m^3\times0.6\right)\times£2.30/m^3 = £226.66/yr$$

Because waste is generated during treatment, this would affect the estimated sewerage saving. The manufacturer did not specify the amount of waste generated, hence it was assumed that the waste generated was 50% of the treatment capacity, thus reducing the sewerage saving to £113/yr.

$$\text{Operating cost} - 0.6kWh/\times£0.15/kWh\times365 = £32.85/yr$$

The energy required to heat the water was determined from the specific heat relationship ($Q = cm\Delta T$). Assuming 300 litres of the 450 litres of water used is heated per day for shower, bathing and hand washing, the energy required to raise the temperature from 8°C to 45°C is;

$$Q = (4186J/kg°C)\times(300kg)\times(45°C - 8°C) = 4.6\times10^7\,J$$

$$4.6\times10^7\,J = \left(\frac{4.6\times10^7}{3.6\times10^6}\right)kWh = 12.78kWh$$

With electricity cost of £0.1/kWh and a 20% reduction in energy cost for water reduction, the amount saved from heat recovery is;

$$\left(\frac{£0.15}{kWh}\times 12.78kWh\right)\times 365 = £699.70/yr$$

$$(£699.70/yr)\times 0.2 = £139.94/yr$$

From these calculations and with an initial purchase cost of £3750, it was estimated that the AquaCycle 900 has a payback period of around 19 years without the Pontos HeatCycle add-on, and 11 years with the add-on. This does not include the installation cost or the replacement of pumps and UV light (replacement required every 10 years), which would increase the payback period.

Waterscan Ltd – GW2000

The GW2000 recycles water used in baths, showers as well as rainwater to flush the toilet, laundry cleaning and irrigation; the system is suitable for use in hotels, leisure centres, large offices and residential blocks. Grey water is initially collected in an aeration tank and the aeration process encourages natural biological cleansing of bio-degradable particles. The water then flows into the filtration tank which contains the patented ultra-filtration membrane. The ultra-filtration membrane is submerged directly into the tank and is the core element in the GW2000. Due to the small pore size of the ultra-filtration membrane, bacteria, viruses and solid soils are held back. The quality of the treated water meets the hygienic requirement of the EU Bathing Water Directive (Waterscan, 2012). The filter plates are aerated to ensure oxygen content in the membrane, which helps to keep the membrane clean. This efficient method of self-cleaning reduces requirement for maintenance as well as the need for chemical cleaning.

The service life of the membrane is around 10 years and the payback period is claimed to be as low as 3 years (Waterscan, 2012). The low payback period may be due to calculations based on usage on a larger scale. It may also be due to the fact that the GW2000 is a qualified water recycling technology published in the Water Technology List. This means businesses that purchases the GW2000 are able to claim enhanced capital allowance. The Enhanced Capital Allowance scheme (ECA) hopes to encourage businesses to invest in water quality improving and water saving technologies, it permits the full cost of the investment to be relieved against taxable income over the period of the investment.

AQUACO Water Recycling Ltd – Aquaco Aerobic Grey water System

The Aquaco Aerobic Grey water System collects bath, shower and hand basin water which is then treated ready for use in toilets, washing machines and irrigation. The system requires no added chemicals and the treated water quality exceeds the hygienic requirement of the EU Bathing Water Directive. The system consist of a settlement tank, water from this tank is fed into an aerobic treatment tank where it is aerated to encourage biological treatment of the bacteria. A patented water lift system then transport the water into the Membrane Bio-Reactor which functions as a secondary aerobic biological treatment, this is followed by a submerged ultra-filtration unit. The small pore size of the membrane enables exclusion of particles, bacteria and viruses (Aquaco Water Recycling Ltd, 2011).

The Aquaco Aerobic Grey water System can process a daily capacity of 1,000 litres to 10,000 litres, promises a saving of up to 50% on water bills and 100% saving of mains water for toilet flushing and laundry, can be combined with rainwater system and is listed on the Water Technology List. Aquaco claims the system can provide a payback period of 3-5 years; this payback period is most likely dependant of the scale at which the system is being used (Aquaco Water Recycling Ltd, 2011).

Brac Systems Inc – Brac Grey water Recycling System

The Brac System collects grey water from showers, baths and laundry, then filters and distributes it for use in toilet flushing. The grey water entering the system is filtered through a 100 Microns pleated filter cartridge. The tank consists of a tri-chlorine tablet which is very similar to the type used in swimming pools. The tablet lasts for approximately 8 weeks and keeps the grey water free from any bacteria and odours. The manufacturer claim the use of the system will save the average household approximately 35% of their total water consumption. Thus, with a purchase cost of £1,750 (Green Building Supply, 2010), the payback period for the RGW350 (350 litres capacity) was calculated as follows;

$$\text{Water saving} - \left(\left(\frac{350\times365}{1000}\right)m^3\times0.35\right)\times£1.20/m^3 = £53.65/yr$$

$$\text{Sewerage saving} - \left(\left(\frac{350\times365}{1000}\right)m^3\times0.35\right)\times£2.30/m^3 = £102.83/yr$$

Based on a four person household and taking sludge production into account, this equates to a payback period of around 17 years. Including other costs such as the installation cost, maintenance cost and operation cost will increase the payback period.

CME Sanitary Systems – Ecoplay Micro Grey water Recycling System

The Ecoplay system uses very simple processes to treat grey water. Grey water from bath and shower is collected in the cleaning tank, surface debris such as hair and soap foam are primarily removed using a skimmer, heavier waste particles naturally sinks to the bottom of the tank and is flushed off to waste. The remaining water in the middle of the tank is then transferred to a storage tank ready for use in toilet flushing. The maximum capacity of the storage tank is 100 litres, enough for approximately 20 flushes. The Ecoplay is completely automated and if the system is not used within 24 hours of regular use, the grey water retained within it would be purged to waste; this aids in cleaning the system and prevents water from going stale. According to the manufacturer, the system can reduce mains water consumption and drainage by up to 30%. The purchasing cost of the device is around £1956 (Discount Build Supplies, 2009), assuming the device was purchased for around £2000 (including delivery cost) and considering the waste to sewerage, the estimated payback period is around 17 years.

Summary

Out of all the systems described above, the one that really stands out is the Ecoplay system due to its simplicity. The Ecoplay requires minimum space and operates just like a normal toilet (cistern and flush plate are built into system), thus eliminating any unnecessary plumbing. The device is very compact and is supplied in a pre-assembled modular arrangement, which means it is easy to install and requires minimal additional work. The Ecoplay has no filters to clean or replace and has one low energy pump for transferring the grey water to the cistern, this means compared to the rest of the system, the Ecoplay requires minimal maintenance. The one disadvantage of the Ecoplay system is the fact that it can only be used for residential homes, and from looking at the other grey water recycling devices, it can be seen that the technology becomes more economical with size, hence the long payback period of around 17 years. Not being able to apply the system for commercial or industrial use means the manufacturer would not be able to attract the wider market where more profits can be made.

Another interesting technology is the Pontos HeatCycle & Pontos AquaCycle grey water recycling system, the concept behind this technology is very similar to the proposed design for this project. The one possible drawback of this technology is sludge production which is flushed to drain and adds to sewerage cost, the Arvia™ process on the other hand does not produce any sludge. The Pontos system is however, proof that incorporating heat recovery into grey water recycling system does increase the economic viability of the grey water recycling technology.

Hansgrohe promises a reduction in the energy cost for hot water preparation by 20%, this can be increased further by integrating a more efficient method of heat recovery to the system. The purchase or upfront capital cost of the Arvia™ process cannot yet be specified for confidentiality reasons but due to the low cost of Nyex™, it is likely that the capital cost would be lower than the cost of a Hansgrohe device. Due to the fact that no waste is generated with the Arvia™ process, the cost savings from water recycling would be around 33% higher when compared to a Hansgrohe device of comparable scale. This indicates that once the Arvia™ process has been successfully designed; it will be a fierce competitor in the grey water recycling market.

REFERENCES

ABBOOD, D. W., MUSTAFA, A. S., & ALI, S. A. K. (2013). Social Investigation of Greywater Reuse in Baghdad. *Civil and Environmental Research*, *3*(12), 132-145.

ABDULLAHA, M. A., CHIANGB, L. & NADMEEM, M. (2009). Comparative evaluation of adsorption kinetics and isotherms of a natural product removal by Amberlite polymeric adsorbents. *Chemical Engineering Journal,* 146**,** 370-376.

ACT GOVERNMENT AUSTRALIA. (2008). *The ACT's water resources management strategy* [Online]. Australia. Available: http://www.thinkwater.act.gov.au/permanent_ measures/the_act_water_strategy.shtml [Accessed September 2012].

AGUADO, J., ARSUAGA, J. M., ARENCIBIA, A., LINDO, M., & GASCÓN, V. (2009). Aqueous heavy metals removal by adsorption on amine-functionalized mesoporous silica. *Journal of Hazardous Materials*, *163*(1), 213-221.

AL-GHOUTI, M. A., KHRAISHEH, M. A. M., ALLEN, S. J., & AHMAD, M. N. (2003). The removal of dyes from textile wastewater: a study of the physical characteristics and adsorption mechanisms of diatomaceous earth. *Journal of Environmental Management*, *69*(3), 229-238.

AL-HAMAIEDEH, H., & BINO, M. (2010). Effect of treated grey water reuse in irrigation on soil and plants. *Desalination*, *256*(1), 115-119.

AL-JAYYOUSI, O. R. (2003). Greywater reuse: towards sustainable water management. *Desalination*, *156*(1), 181-192.

AL-WABEL, M. I. (2011). Simple system for handling and reuse of gray water resulted from ablution in Mosques of Riyadh City, Saudi Arabia. In *Proceedings of International Conference on Environment Science and Engineering, IPCBEE* (Vol. 8).

ALCAMO, J., HENRICHS, T., & ROSCH, T. (2000). World water in 2025: Global modeling and scenario analysis. *World water scenarios analyses*.

ALCAMO, J., DÖLL, P., HENRICHS, T., KASPAR, F., LEHNER, B., RÖSCH, T. AND SIEBERT, S. (2003). Global estimates of water withdrawals and availability under current and future "business-as-usual" conditions. *Hydrological Sciences Journal*, *48*(3), 339-348.

ALMEIDA, M. C., BUTLER, D., & FRIEDLER, E. (1999). At-source domestic wastewater quality. *Urban water*, *1*(1), 49-55.

ANDRZEJEWSKA, A., KRYSZTAFKIEWICZ, A., & JESIONOWSKI, T. (2007). Treatment of textile dye wastewater using modified silica. *Dyes and pigments*, *75*(1), 116-124.

ANGELAKIS, A. N., & DURHAM, B. (2008). Water recycling and reuse in EUREAU countries: Trends and challenges. *Desalination*, *218*(1), 3-12.

ANGLADA, A., URTIAGA, A., & ORTIZ, I. (2009). Contributions of electrochemical oxidation to waste-water treatment: fundamentals and review of applications. *Journal of chemical technology and biotechnology*, *84*(12), 1747-1755.

ANTONOPOULOU, G., KIRKOU, A., & STASINAKIS, A. S. (2013). Quantitative and qualitative greywater characterization in Greek households and investigation of their treatment using physicochemical methods. *Science of the Total Environment*, *454*, 426-432.

AQUAOX. (2014). Hypochlorous Acid, Sodium Hypochlorite and Chlorine; Electrolyzed Water. [ONLINE] Available at: https://aquaox.wordpress.com/category/hypochlorous-acid-sodium-hypochlorite-and-chlorine/. [Accessed 15 April 2014].

ARIKA, M., KOBAYASHI, H. & KIHARA, H. (1966). Pilot plant test of an activated sludge ultrafiltration combined process for domestic wastewater reclamation. *Desalination,* 23**,** 77-86.

AROUA, M. K., LEONG, S. P. P., TEO, L. Y., YIN, C. Y., MOHD, W. & DAUD, A. W. (2008). Real-time determination of kinetics of adsorption of lead(II) onto palm shell-based activated carbon using ion selective electrode. *Bioresource Technology,* 99**,** 5786–5792.

ASADA, T., OHKUBO, T., KAWATA, K., & OIKAWA, K. (2006). Ammonia adsorption on bamboo charcoal with acid treatment. *Journal of health science*, *52*(5), 585-589.

ASGHAR, H. M. A., HUSSAIN, S. N., ROBERTS, E. P. L., BROWN, N. W., & SATTAR, H. (2012a). Development of composite adsorbent for wastewater treatment using adsorption and electrochemical regeneration. *Proceedings of the world academy of science, engineering & technology*, *72*, 2012.

ASGHAR, H. M. A., ROBERTS, E. P. L., & BROWN, N. W. (2012b). Disinfection of Water by Adsorption with Electrochemical Regeneration. World Academy of Science, Engineering and Technology, 6, 12-21.

ASGHAR, H. M. A., HUSSAIN, S. N., ROBERTS, E. P. L., BROWN, N. W., & SATTAR, H. (2013). GIC-Based Adsorbents for Wastewater Treatment through Adsorption and Electrochemical-Regeneration.

ASGHAR, H. M. A., HUSSAIN, S. N., SATTAR, H., BROWN, N. W., & ROBERTS, E. P. L. (2014). Mercaptan's Removal from Aqueous Solution Using Modified Graphite Based Adsorbent Through Batch-Wise Adsorption-Regeneration. *Chemical Engineering Communications*.

ATLAS, R. M. (1984). Sanitation and Disease-Health Aspects of Excreta and Waste-water Management. *JAWRA Journal of the American Water Resources Association*, *20*(5), 803-803.

ATWATER, R. (1998). Urban water recycling feasibility assessment handbook. Bookman Edmonston Engineering Inc, California Urban Water Agencies, 1-2.

AUSTRALIAN CAPITAL TERRITORY, CANBERRA 2007. Grey water Use: Guidelines for residential properties in Canberra. *Treatment of grey water.* Australia: Australian Capital Territory, Canberra.

AUSTRALIAN GOVERNMENT DEPARTMENT OF THE ENVIRONMENT, WATER, HERITAGE AND THE ARTS, 2010. Securing our Water Future. *The path to water reform in Australia.* Australia: Australian Government Department of the Environment, Water, Heritage and the Arts.

BAEK, N. C., SHIN, U. C., & YOON, J. H. (2005). A study on the design and analysis of a heat pump heating system using wastewater as a heat source. *Solar Energy*, *78*(3), 427-440.

BANDE, R. M., PRASAD, B., MISHRA, I. M., & WASEWAR, K. L. (2008). Oil field effluent water treatment for safe disposal by electroflotation. *Chemical Engineering Journal*, *137*(3), 503-509.

BANI-MELHEM, K., & SMITH, E. (2012). Grey water treatment by a continuous process of an electrocoagulation unit and a submerged membrane bioreactor system. *Chemical Engineering Journal*, *198*, 201-210.

BANSAL, R. C., & GOYAL, M. (2010). *Activated carbon adsorption*. CRC press.

BANSODE, R. R. (2002). *Treatment of organic and inorganic pollutants in municipal wastewater by agricultural by-product based granular activated carbons (GAC)* (Doctoral dissertation, Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in The Department of Food Science by Rishipal Rastrapal Bansode B. Tech., Osmania University).

BARD, A. J., AND FAULKNER, L. R. (2000). Electrochemical methods: Fundamentals and Applications (Vol. 2). New York: Wiley.

BARROS, M. A. S. D., ARROYO, P. A., & SILVA, E. A. (2013). General Aspects of Aqueous Sorption Process in Fixed Beds.

BAZAN, J. C., & BISANG, J. M. (2004). Electrochemical removal of tin from dilute aqueous sulfate solutions using a rotating cylinder electrode of expanded metal. *Journal of applied electrochemistry*, *34*(5), 501-506.

BEJANKIWAR, R. S. (2002). Electrochemical treatment of cigarette industry wastewater: feasibility study. *Water research*, *36*(17), 4386-4390.

BELASH, I. T., ZHARIKOV, O. V., & PALNICHENKO, A. V. (1990). Synthesis, stability and structure of GIC with Li, Na and K. *Synthetic Metals*, *34*(1), 47-52.

BENAMI, M., GILLOR, O., & GROSS, A. (2015). The question of pathogen quantification in disinfected graywater. *Science of The Total Environment*, *506*, 496-504.

BERENGUER, R., MARCO-LOZAR, J. P., QUIJADA, C., CAZORLA-AMOROS, D., & MORALLÓN, E. (2010). Comparison among Chemical, Thermal, and Electrochemical Regeneration of Phenol-Saturated Activated Carbon†. *Energy & Fuels*, *24*(6), 3366-3372.

BERGMANN, M. E. H., & KOPARAL, A. S. (2005). Studies on electrochemical disinfectant production using anodes containing RuO2. *Journal of applied electrochemistry*, *35*(12), 1321-1329.

BIRKS, R. (1998). *Biological aerated filters and membranes for grey water treatment.* MSc Thesis, Cranfield University.

BIRKS, R., & HILLS, S. (2007). Characterisation of indicator organisms and pathogens in domestic greywater for recycling. *Environmental monitoring and assessment*, *129*(1-3), pp 61-69.

BISWAS, N., & LAZARESCU, G. (1991). Removal of oil from emulsions using electrocoagulation. *International journal of environmental studies*, *38*(1), 65-75.

BOEHM, H. P., SETTON, R., & STUMPP, E. (1994a). Nomenclature and terminology of graphite intercalation compounds (IUPAC Recommendations 1994). *Pure and Applied Chemistry*, *66*(9), 1893-1901.

BOEHM, H. P. (1994b). Some aspects of the surface chemistry of carbon blacks and other carbons. *Carbon*, *32*(5), 759-769.

BOGARDI, J. J., DRUDGEON, D., LAWFORD, R., FLINKERBUSCH, E., MEYN, A., PAHL-WOSTL, C., VIELHAUER, K., VÖRÖSMARTY, C. (2012). Water security for a planet under pressure: interconnected challenges of a changing world call for sustainable solutions. *Current Opinion in Environmental Sustainability*, *4*(1), 35-43.

BOHART, G. S., AND ADAMS, E. Q. (1920). Some aspects of the behavior of charcoal with respect to chlorine. 1. *Journal of the American Chemical Society*, *42*(3), 523-544.

BOLZ, F. (1977). *Advanced Materials in Catalysis*. Elsevier.

BOORMAN, G. A. (1999). Drinking water disinfection byproducts: review and approach to toxicity evaluation. *Environmental Health Perspectives*, *107*(Suppl 1), 207.

BOTTANI, E. J., & TASCÓN, J. M. (Eds.). (2011). *Adsorption by carbons: novel carbon adsorbents*. Elsevier.

BOUAZIZ, I., HAMZA, M., ABDELHEDI, R., SAVALL, A., & SERRANO, K. G. (2014). Treatment of Diluted Solutions of Methylene Blue by Adsorption Coupled with

Electrochemical Regeneration: A Comparative Study of Three Adsorbants. *ECS Transactions*, *59*(1), 495-502.

BOYD, G. E., ADAMSON, A. W. & MYERS, L. S. J. (1947). The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. II. Kinetics. *Journal of the American Chemical Society,* 69**,** 2836-2848.

BRANDT, N. B., CHUDINOV, S. M., & PONOMAREV, Y. G. (Eds.). (2012). *Semimetals: 1. Graphite and its Compounds*. Elsevier.

BREWER, D., BROWN, R. & STANFIELD, G. (2001). *Rainwater and grey water in buildings: project report and case studies,* UK, BSRIA.

BRITISH STANDARDS INSTITUTION. (2009). 8515: 2009–Rainwater Harvesting Systems–Code of Practice. *British Standard Institution, UK*.

BRITISH STANDARDS INSTITUTION. (2010). 8525–1: 2010 Greywater systems—Part 1: Code of practice, BSI. *British Standards Institution, UK*.

BRITISH STANDARDS INSTITUTION. (2011). 8525-2: 2011 Greywater systems—Part 2: Domestic greywater treatment equipment – Requirements and test methods, BSI. *British Standards Institution, UK*.

BRODIE, B. C. (1859). On the atomic weight of graphite. *Philosophical Transactions of the Royal Society of London*, 249-259.

BROWN, N. W., ROBERTS, E. P. L., CHASIOTIS, A., CHERDRON, T., & SANGHRAJKA, N. (2004a). Atrazine removal using adsorption and electrochemical regeneration. *Water research*, *38*(13), 3067-3074.

BROWN, N. W., ROBERTS, E. P. L., GARFORTH, A. A., & DRYFE, R. A. W. (2004b). Electrochemical regeneration of a carbon-based adsorbent loaded with crystal violet dye. *Electrochimica acta*, *49*(20), 3269-3281.

BROWN, N.W. (2005). Adsorption and electrochemical regeneration for wastewater treatment–development of a process, PhD thesis, University of Manchester.

BROWN, N. W., & ROBERTS, E. P. L. (2007). Electrochemical pre-treatment of effluents containing chlorinated compounds using an adsorbent. *Journal of Applied Electrochemistry*, *37*(11), 1329-1335.

BROWN, N. W., ROBERTS, E. P. L., HUSSAIN, S. N., DE-LAS-HERAS, N., GAFFEY, P. GAFFEY, A. KEIGHLEY, M. (2008). Development of Grey Water Treatment System. *JAMA-Journal of the American Medical Association*, *299*(18), 2128-2128.

BROWN, N. W., & ROBERTS, E. P. L. (2013). Combining adsorption with anodic oxidation as an innovative technique for removal and destruction of organics. *Water Science & Technology*, *68*(6), 1216-1222.

BRUNAUER, S., EMMETT, P. H., & TELLER, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*(2), 309-319.

CAMPBELL, D. A., DALRYMPLE, I. M., SUNDERLAND, J. G., & TILSTON, D. (1994). The electrochemical recovery of metals from effluent and process streams. *Resources, Conservation and Recycling*, *10*(1), 25-33.

CAMPISANO, A., AND MODICA, C. (2010). Experimental investigation on water saving by the reuse of washbasin grey water for toilet flushing. *Urban Water Journal*, *7*(1), 17-24.

CANIZARES, P., DOMINGUEZ, J. A., RODRIGO, M. A., VILLASENOR, J., & RODRIGUEZ, J. (1999). Effect of the current intensity in the electrochemical oxidation of aqueous phenol wastes at an activated carbon and steel anode. *Industrial & engineering chemistry research*, *38*(10), 3779-3785.

CANIZARES, P., GARCIA-GOMEZ, J., SAEZ, C., & RODRIGO, M. A. (2003). Electrochemical oxidation of several chlorophenols on diamond electrodes Part I. Reaction mechanism. *Journal of applied electrochemistry*, *33*(10), 917-927.

CANIZARES, P., LOBATO, J., PAZ, R., RODRIGO, M. A., & SÁEZ, C. (2005). Electrochemical oxidation of phenolic wastes with boron-doped diamond anodes. *Water Research*, *39*(12), 2687-2703.

CANIZARES, P., MARTÍNEZ, F., JIMÉNEZ, C., LOBATO, J., & RODRIGO, M. A. (2006). Coagulation and electrocoagulation of wastes polluted with dyes. *Environmental science & technology*, *40*(20), 6418-6424.

CANADA MORTGAGE AND HOUSING CORPORATION. (2002). *Rainwater Harvesting and Grey Water Reuse* [Online]. Canada. Available: http://www.cmhc-schl.gc.ca/publications/en/rh-pr/tech/03-100-e.htm.

CAPITAL REGIONAL DISTRICT. (2004). Greywater Reuse Study Report. Available: http://www.crd.bc.ca/9557CE50-D7B9-4F83-8A01-8405358C7A2D/FinalDownload/DownloadId-C4D090A9D0C77A6685B57ADACC796C61/9557CE50-D7B9-4F83-8A01-8405358C7A2D/reports/water_/2004_/crdgreywaterreusestu-1/crdgreywaterreusestu.pdf [Accessed July 2012].

CARBTROL® Corporation. (1992). Granular Activated Carbon for Water & Wastewater Treatment. Rev.10/92, TP-3

CHARLIER, A., CHARLIER, M. F., & FRISTOT, D. (1989). Binary graphite intercalation compounds. *Journal of Physics and Chemistry of Solids*, *50*(10), 987-996.

CHATZISYMEON, E., XEKOUKOULOTAKIS, N. P., COZ, A., KALOGERAKIS, N., & MANTZAVINOS, D. (2006). Electrochemical treatment of textile dyes and dyehouse effluents. *Journal of hazardous materials*, *137*(2), 998-1007.

CHEN, G., CHEN, X., & YUE, P. L. (2000). Electrocoagulation and electroflotation of restaurant wastewater. *Journal of environmental engineering*, *126*(9), 858-863.

CHEN, G., WU, D., WENG, W., & WU, C. (2003). Exfoliation of graphite flake and its nanocomposites. *Carbon*, *41*(3), 619-621.

CHEN, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and purification Technology*, *38*(1), 11-41.

CHRISTOVA-BOAL, D., EDEN, R. E., & MCFARLANE, S. (1996). An investigation into greywater reuse for urban residential properties. *Desalination*, *106*(1), 391-397.

CHUNG, D. D. L. (1987). Exfoliation of graphite. *Journal of materials science*, *22*(12), 4190-4198.

CHUNG, D. D. L. (2002). Review graphite. *Journal of materials science*, *37*(8), 1475-1489.

CITY OF OLYMPIA. (2014). Reclaimed Water. [online] Available at: http://olympiawa.gov/city-utilities/reclaimed-water.aspx [Accessed 20 Nov. 2013].

COMMITTEE on CLIMATE CHANGE (2014) Energy prices and bills, UK: Committee on Climate Change.

COMNINELLIS, C. (1994). Electrocatalysis in the electrochemical conversion/combustion of organic pollutants for waste water treatment. *Electrochimica Acta*, *39*(11), 1857-1862.

CONTE Jr, A. A. (1983). Graphite intercalation compounds as solid lubricants. *ASLE transactions*, *26*(2), 200-208.

CONTI-RAMSDEN, M. G., ASGHAR, H. M. A., HUSSAIN, S. N., ROBERTS, E. P. L., & BROWN, N. W. (2012a). Removal of mercaptans from a gas stream using continuous adsorption-regeneration. *Water Science & Technology*, *66*(9), 1849-1855.

CONTI-RAMSDEN, M. G., BROWN, N. W., & ROBERTS, E. P. (2012b). Towards an odour control system combining slurry sorption and electrochemical regeneration. *Chemical Engineering Science*, *79*, 219-227.

COONEY, D. O. (1999). Adsorption Design for Wastewater Treatment. Florida: CRC Press LLC.

COSGROVE, W. J., & RIJSBERMAN, F. R. (2014). *World water vision: making water everybody's business*. Routledge.

COSTA, C., & RODRIGUES, A. (1985). Design of cyclic fixed-bed adsorption processes. Part I: Phenol adsorption on polymeric adsorbents. *AIChE journal*, *31*(10), 1645-1654.

COULSON, J. M., RICHARDSON, J. F., BACKHURST, J. R., & HARKER, J. H. (1996). Fluid flow, heat transfer and mass transfer. *Filtration & Separation*, *33*(2), 102.

COUTO, E. D. A., CALIJURI, M. L., ASSEMANY, P. P., DA FONSECA SANTIAGO, A., & LOPES, L. S. (2014). Greywater treatment in airports using anaerobic filter followed by UV disinfection: an efficient and low cost alternative. *Journal of Cleaner Production*.

CRITTENDEN, J. C., & WEBER, W. J. (1978). Predictive model for design of fixed-bed adsorbers: Parameter estimation and model development. *Journal of the Environmental Engineering Division*, *104*(2), 185-197.

CRITTENDEN, J. C., HUTZLER, N. J., GEYER, D. G., ORAVITZ, J. L., & FRIEDMAN, G. (1986). Transport of organic compounds with saturated groundwater flow: Model development and parameter sensitivity. *Water Resources Research*, *22*(3), 271-284.

CROOK, J., AND SURAMPALLI, R. (2005). Water reuse criteria in the United States. *Water Supply*, *5*(3-4), 1-7.

DĄBROWSKI, A. (2001). Adsorption—from theory to practice. *Advances in colloid and interface science*, *93*(1), 135-224.

DAIFULLAH, A. A. M., GIRGIS, B. S., & GAD, H. M. H. (2004). A study of the factors affecting the removal of humic acid by activated carbon prepared from biomass material. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *235*(1), 1-10.

DALAHMEH, S. (2013). Bark and charcoal filters for greywater treatment.

DAS, D., GAUR, V. & VERMA, N. (2004). Removal of volatile organic compound by activated carbon fiber. *Carbon,* 42**,** 2949-2962.

DECC, DEPARTMENT OF ENERGY AND CLIMATE CHANGE (2012). Estimates of heat use in the United kingdom in 2011: Domestic Energy Consumption in the UK between 1970 and 2013. Department of Energy and Climate Change, UK.

DEPARTMENT FOR COMMUNITIES AND LOCAL GOVERNMENT. (2009). The Water Efficiency Calculator for new dwellings. Available: http://www.planningportal.gov.uk/ uploads/br/water_efficiency_calculator.pdf [Accessed April 2012].

DERMENTZIS, K., & OUZOUNIS, K. (2008). Continuous capacitive deionization–electrodialysis reversal through electrostatic shielding for desalination and deionization of water. *Electrochimica Acta*, *53*(24), 7123-7130.

DHAR, H. P., HOWELL, D. W., & BOCKRIS, J. M. (1982). The use of in situ electrochemical reduction of oxygen in the diminution of adsorbed bacteria on metals in seawater. *Journal of the Electrochemical Society*, *129*(10), 2178-2182.

DIAPER, C., DIXON, A., BUTLER, D., FEWKES, A., PARSONS, S.A., STEPHENSON, T., STRATHERN, M., & STRUTT, J. (2001). Small scale water recycling systems – risk assessment and modelling. Wat. Sci. Tech., 43(10), 83–90.

DIXON, A.M., BUTLER, D., & FEWKES, A. (1999). Guidelines for Greywater Re-Use: Health Issues, Wat. and Env. Manage., 13(5), 322–326.

DO, D. D. (1998). Adsorption Analysis: Equilibria and Kinetics (Chemical Engineer Series, Volume 2). Edition. Imperial College Press.

DOMINGO-GARCIA, M., GROSZEK, A. J., LÓPEZ-GARZÓN, F. J., & PÉREZ-MENDOZA, M. (2002). Dynamic adsorption of ammonia on activated carbons measured by flow microcalorimetry. *Applied Catalysis A: General*, *233*(1), 141-150.

DREYER, D. R., PARK, S., BIELAWSKI, C. W., & RUOFF, R. S. (2010). The chemistry of graphene oxide. *Chemical Society Reviews*, *39*(1), 228-240.

DU, X. L., YUAN, Q. P., & LI, Y. (2008). Mathematical analysis of solanesol adsorption on macroporous resins using the general rate model. *Chemical engineering & technology*, *31*(9), 1310-1318.

EMERYA, N., HÉROLDA, C., & LAGRANGE, P. (2009). *Superconducting intercalated graphite*. Nova Science Publishers.

ENGLERT, A. H. & RUBIO, J. (2005). Characterization and environmental application of a Chilean natural zeolite. *International Journal of Mineral Processing,* 75**,** 21–29.

ENOKI, T., SUZUKI, M., & ENDO, M. (2003). Graphite intercalation compounds and applications. *Oxford University Press*.

ENVIRONMENTAL AGENCY. (2011). Greywater for domestic users: an information guide. [Accessed February 2012].

ENVIRONMENTAL PROTECTION AGENCY (EPA) 2004. Guidelines for water reuse. *In:* U.S. *Agency for International Development* (ed.). Washington, DC, USA.

ERIKSSON, E., AUFFARTH, K., HENZE, M., & LEDIN, A. (2002). Characteristics of grey wastewater. *Urban water*, *4*(1), 85-104.

ERIKSSON, E., ANDERSEN, H. R., MADSEN, T. S., & LEDIN, A. (2009). Greywater pollution variability and loadings. *Ecological engineering*, *35*(5), 661-669.

ERVAN, Y., & WENTEN, I. G. (2002). Study on the influence of applied voltage and feed concentration on the performance of electrodeionization. *Songklanakarin J. Sci. Technol*, *24*, 955-963.

ESLAMI-NEJAD, P., & BERNIER, M. (2009). Impact of grey water heat recovery on the electrical demand of domestic hot water heaters. In *Proceedings: 11th international building performance simulation association conference and exhibition* (pp. 681-687).

EUROPEAN COMMISSION. (2011). Analysis of grey water reuse considers pollutant management. *Science for Environment Policy* [Online]. Available: http://ec.europa.eu/environment/integration/research/newsalert/pdf/232na5.pdf [Accessed August 2012].

EUROPEAN ENVIRONMENT AGENCY (EEA). (2014). Water stress - European Environment Agency (EEA). [ONLINE] Available at: http://www.eea.europa.eu/themes/water/wise-help-centre/glossary-definitions/water-stress. [Accessed 28 October 2014].

EXCELL, G., J. A. HUGHES, AND J. G. SUNDERLAND. (1989). The electrochemical production of graphite bi-sulphate. Confidential Report 3429, Electricity Council Research Centre, Capenhurst.

FABRIZI, L. (2014). Drought and water shortage - Lenntech. [ONLINE] Available at: http://www.lenntech.com/water-shortage.htm. [Accessed 28 October 2014].

FALKENMARK, M. (1989). The massive water scarcity now threatening Africa: why isn't it being addressed?. *Ambio*, 112-118.

FARUQUI, N., & AL-JAYYOUSI, O. (2002). Greywater reuse in urban agriculture for poverty alleviation: a case study in Jordan. *Water International*, *27*(3), 387-394.

FAUST, S. D., & ALY, O. M. (1987). *Adsorption processes for water treatment*. Massachusetts: Butterworth.

FAUST, S. D., & ALY, O. M. (1998). *Chemistry of water treatment*. CRC Press.

FISCHER, J. E. (1980). Graphite intercalation compounds: Electronic properties and their correlation with chemistry. *Physica B+C*, *99*(1), 383-394.

FOO, K. Y. & HAMEED, B. H. (2010). Insights into the modeling of adsorption isotherm systems. *Chemical Engineering Journal,* 156**,** 2-10.

FOURNEL, L., MOCHO, P., BROWN, R., & LE CLOIREC, P. (2010). Modeling breakthrough curves of volatile organic compounds on activated carbon fibers. *Adsorption*, *16*(3), 147-153.

FRAITURE, C., WICHELNS, D., KEMP BENEDICT, E. & ROCKSTROM, J. (2007). Scenarios on water for food and environment. In Water for Food, Water for Life: A

Comprehensive Assessment of Water Management in Agriculture, Chapter 3, Earthscan, London and International Water Management Institute, Colombo.

FRANKLIN, R. E. (1951). Crystallite growth in graphitizing and non-graphitizing carbons. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, *209*(1097), 196-218.

FRIEDLER, E. (2004). Quality of individual domestic greywater streams and its implication for on-site treatment and reuse possibilities. *Environmental technology*, *25*(9), 997-1008.

FRIEDLER, E., KOVALIO, R., & GALIL, N. I. (2005). On-site greywater treatment and reuse in multi-storey buildings. *Water Science & Technology*, *51*(10), 187-194.

FRIEDLER, E., & HADARI, M. (2006). Economic feasibility of on-site greywater reuse in multi-storey buildings. *Desalination*, *190*(1), 221-234.

FRIEDLER, E., KATZ, I., & DOSORETZ, C. G. (2008). Chlorination and coagulation as pretreatments for greywater desalination. *Desalination*, *222*(1), 38-49.

FRIEDLER, E., & GILBOA, Y. (2010). Performance of UV disinfection and the microbial quality of greywater effluent along a reuse system for toilet flushing. *Science of the total environment*, *408*(9), 2109-2117.

GANZI, G. C., WOOD, J. H., & GRIFFIN, C. S. (1992). Water purification and recycling using the CDI process. *Environmental Progress*, *11*(1), 49-53.

GAO, P., CHEN, X., SHEN, F., & CHEN, G. (2005). Removal of chromium (VI) from wastewater by combined electrocoagulation–electroflotation without a filter. *Separation and Purification Technology*, *43*(2), 117-123.

GARG, V. K., AMITA, M., KUMAR, R., & GUPTA, R. (2004). Basic dye (methylene blue) removal from simulated wastewater by adsorption using Indian Rosewood sawdust: a timber industry waste. *Dyes and pigments*, *63*(3), 243-250.

GARNETT, P. J., AND TREAGUST, D. F. (1992). Conceptual difficulties experienced by senior high school students of electrochemistry: Electrochemical (galvanic) and electrolytic cells. *Journal of Research in Science Teaching*, *29*(10), 1079-1099.

GE, J., QU, J., LEI, P., & LIU, H. (2004). New bipolar electrocoagulation–electroflotation process for the treatment of laundry wastewater. *Separation and Purification Technology*, *36*(1), 33-39.

GEARY, P.M., STAFFORD, D. AND WHITEHEAD J.H. (2005). On-site Domestic Wastewater Treatment and Reuse, BDP Environmental Design Guide DES 24. Royal Australian Institute of Architects, February 2005.

GERENTE, C., LEE, V., LE CLOIREC, P. & MCKAY, G. (2007). Application of Chitosan for the Removal of Metals from Wastewaters by Adsorption—Mechanisms and Models Review. *Critical Reviews in Environmental Science and Technology,* 37**,** 41 -127.

GHERARDINI, L., MICHAUD, P. A., PANIZZA, M., COMNINELLIS, C., & VATISTAS, N. (2001). Electrochemical oxidation of 4-chlorophenol for wastewater treatment: definition of normalized current efficiency (ϕ). *Journal of the Electrochemical Society*, *148*(6), D78-D82.

GHISI, E., AND FERREIRA, D. F. (2007). Potential for potable water savings by using rainwater and greywater in a multi-storey residential building in southern Brazil. *Building and Environment*, *42*(7), 2512-2522.

GILBOA, Y., & FRIEDLER, E. (2008). UV disinfection of RBC-treated light greywater effluent: Kinetics, survival and regrowth of selected microorganisms. *Water research*, *42*(4), 1043-1050.

GILES, C. H., MACEWAN, T. H., NAKHWA, S. N., & SMITH, D. (1960). 786. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *J. chem. Soc.*, 3973-3993.

GLOBAL WATER FORUM. (2012). Understanding water scarcity: Definitions and measurements. [online] Available at: http://www.globalwaterforum.org/2012/05/07/understanding-water-scarcity-definitions-and-measurements/ [Accessed 18 Nov. 2013].

GLUECKAUF, E. (1955). Theory of chromatography. Part 10.—Formulæ for diffusion into spheres and their application to chromatography. *Transactions of the Faraday Society*, *51*, 1540-1551.

GODFREY, S., LABHASETWAR, P., & WATE, S. (2009). Greywater reuse in residential schools in Madhya Pradesh, India—A case study of cost–benefit analysis. *Resources, Conservation and Recycling*, *53*(5), 287-293.

GOVERNMENT OF WESTERN AUSTRALIA, DEPARTMENT OF HEALTH. (2010). Code of Practice for the Reuse of Grey water in Western Australia. *Guide to Reusing Grey water.* Australia: Government of Western Australia,, Department of Health,.

GOSHADROU, A., & MOHEB, A. (2011). Continuous fixed bed adsorption of C.I. Acid Blue 92 by exfoliated graphite: An experimental and modeling study. *Desalination*, *269*(1), 170-176.

GOYAL, M., AND BANSAL, R. C. (2005). *Activated Carbon Adsorption*. CRC Press.

GRIMSHAW, J. (2000) Electrochemical reactions and mechanisms in organic chemistry, Amsterdam. Elsevier Science, 1st edition.

GROSS, A., KAPLAN, D., & BAKER, K. (2007). Removal of chemical and microbiological contaminants from domestic greywater using a recycled vertical flow bioreactor (RVFB). *Ecological engineering*, *31*(2), 107-114.

GUAL, M., MOIÀ, A., & MARCH, J. G. (2008). Monitoring of an indoor pilot plant for osmosis rejection and greywater reuse to flush toilets in a hotel. *Desalination*, *219*(1), 81-88.

GUINEA, E., ARIAS, C., CABOT, P. L., GARRIDO, J. A., RODRÍGUEZ, R. M., CENTELLAS, F., & BRILLAS, E. (2008). Mineralization of salicylic acid in acidic aqueous medium by electrochemical advanced oxidation processes using platinum and boron-doped diamond as anode and cathodically generated hydrogen peroxide. *Water research*, *42*(1), 499-511.

GULYAS, H., CHOROMANSKI, P., MUELLING, N., & FURMANSKA, M. (2009). Toward chemical-free reclamation of biologically pretreated greywater: solar photocatalytic oxidation with powdered activated carbon. *Journal of Cleaner Production*, *17*(13), 1223-1227.

GÜNTHER, F. (2000). Wastewater treatment by greywater separation: Outline for a biologically based greywater purification plant in Sweden. *Ecological Engineering*, *15*(1), 139-146.

GUPTA, S. S., SREEPRASAD, T. S., MALIYEKKAL, S. M., DAS, S. K., & PRADEEP, T. (2012). Graphene from sugar and its application in water purification. *ACS applied materials & interfaces*, *4*(8), 4156-4163.

HALL, J., BATTEN, C. & WILKINS, J. (1974). Domestic Wash Water Reclamation for Reuse as Commode Water Supply Using a Filtration—Reverse Osmosis Technique. *NASA, Langley Research Centre, Hampton*.

HAMDI, M., DOĞAN, M. & ALKAN, M. (2010). Kinetic analysis of reactive blue 221 adsorption on kaolinite. *Desalination,* 256**,** 154-165.

HAMMAMI, S., BELLAKHAL, N., OTURAN, N., OTURAN, M. A., & DACHRAOUI, M. (2008). Degradation of Acid Orange 7 by electrochemically generated •OH radicals in acidic aqueous medium using a boron-doped diamond or platinum anode: A mechanistic study. *Chemosphere*, *73*(5), 678-684.

HARRY, I. D., SAHA, B., & CUMMING, I. W. (2007). Surface properties of electrochemically oxidised viscose rayon based carbon fibres. *Carbon*, *45*(4), 766-774.

HARTONO, T., WANG, S., MA, Q., & ZHU, Z. (2009). Layer structured graphite oxide as a novel adsorbent for humic acid removal from aqueous solution. *Journal of colloid and interface science*, *333*(1), 114-119.

HERNÁNDEZ LEAL, L., TEMMINK, H., ZEEMAN, G. & BUISMAN, C. J. N. (2010). Comparison of three systems for biological greywater treatment. *Water,* 2**,** 155-169.

HO, C. C., AND CHAN, C. Y. (1986). The application of lead dioxide-coated titanium anode in the electroflotation of palm oil mill effluent. *Water research*, *20*(12), 1523-1527.

HO, Y. & MCKAY, G. (1998). Kinetic models for the sorption of dye from aqueous solution by wood. *Trans. IChemE,* 76**,** 183-191.

HO, Y. S. & MCKAY, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry,* 34**,** 451-465.

HO, Y. S., MCKAY, G., WASE, D. A. J. & FORSTER, C. F. (2000). Study of the Sorption of Divalent Metal Ions on to Peat. *Adsorption Science & Technology,* 18**,** 639-650.

HOLDICH, R. G. (2002). *Fundamentals of particle technology*. Midland Information Technology and Publishing.

HOSNY, A. Y. (1992). Separation of oil from oil/water emulsions using an electroflotation cell with insoluble electrodes. *Filtration & separation*, *29*(5), 419-423.

HOSNY, A. Y. (1996). Separating oil from oil-water emulsions by electroflotation technique. *Separations Technology*, *6*(1), 9-17.

HUANG, C. C., LI, H. S., & CHEN, C. H. (2008). Effect of surface acidic oxides of activated carbon on adsorption of ammonia. *Journal of hazardous materials*, *159*(2), 523-527.

HUANG, L., OU, Z., BOVING, T. B., TYSON, J., & XING, B. (2009). Sorption of copper by chemically modified aspen wood fibers. *Chemosphere*, *76*(8), 1056-1061.

HUSSAIN, S.N. (2012). Wastewater treatment by adsorption using graphite adsorbents with electrochemical regeneration, PhD thesis, University of Manchester.

HUSSAIN, S. N., ROBERTS, E. P. L., ASGHAR, H. M. A., CAMPEN, A. K., & BROWN, N. W. (2013). Oxidation of phenol and the adsorption of breakdown products using a graphite adsorbent with electrochemical regeneration. *Electrochimica acta*, *92*, 20-30.

HYPES, W. D., BATTEN, C. E. & WILKINS, J. R. (1975). Processing of combined domestic bath and laundry waste waters for reuse as commode flushing water. *Technical Report NASA TN D-7937*.

INAGAKI, M., IWASHITA, N., & KOUNO, E. (1990). Potential change with intercalation of sulfuric acid into graphite by chemical oxidation. *Carbon*, *28*(1), 49-55.

INCROPERA, F. P. (2011). *Fundamentals of heat and mass transfer*. John Wiley & Sons.

INIESTA, J., MICHAUD, P. A., PANIZZA, M., CERISOLA, G., ALDAZ, A., & COMNINELLIS, C. (2001). Electrochemical oxidation of phenol at boron-doped diamond electrode. *Electrochimica Acta*, *46*(23), 3573-3578.

INOUE, H., KAGOSHIMA, M., YAMASAKI, M., & HONDA, Y. (2004). Radioactive iodine waste treatment using electrodialysis with an anion exchange paper membrane. *Applied radiation and isotopes*, *61*(6), 1189-1193.

ISRAILIDES, C. J., VLYSSIDES, A. G., MOURAFETI, V. N., & KARVOUNI, G. (1997). Olive oil wastewater treatment with the use of an electrolysis system. *Bioresource Technology*, *61*(2), 163-170.

ITAYAMA, T., KIJI, M., SUETSUGU, A., TANAKA, N., SAITO, T., IWAMI, N., MIZUOCHI, M. & INAMORI, Y. (2006). On site experiments of the slanted soil treatment systems for domestic gray water. *Water Science & Technology,* 53**,** 193-201.

IWASAWA, A., HARANO, A., AKIYAMA, Y., NAKAMURA, Y., & NISHIMOTO, Y. (2009). The pH influence of hypochlorous acid on bactericidal effects. *Bokin Bobai-Journal of Antibacterial and Antifungal Agents*, *37*(4), 243-252.

JABORNIG, S., & FAVERO, E. (2013). Single household greywater treatment with a moving bed biofilm membrane reactor (MBBMR). *Journal of Membrane Science*, *446*, 277-285.

JAMRAH, A., AL-OMARI, A., AL-QASEM, L., & GHANI, N. A. (2006). Assessment of availability and characteristics of greywater in Amman. *Water international*, *31*(2), 210-220.

JAMRAH, A., AL-FUTAISI, A., PRATHAPAR, S., & AL HARRASI, A. (2008a). Evaluating greywater reuse potential for sustainable water resources management in Oman. *Environmental monitoring and assessment*, *137*(1-3), 315-327.

JAMRAH, A., & AYYASH, S. (2008b). Greywater Generation and Characterization in Major Cities in Jordan. *Jordan Journal of Civil Engineering*, *2*(4), 376-390.

JEFFERSON, B., LAINE, A., PARSONS, S., STEPHENSON, T., & JUDD, S. (2000). Technologies for domestic wastewater recycling. *Urban water*, *1*(4), 285-292.

JEONG, J., KIM, J. Y., & YOON, J. (2006). The role of reactive oxygen species in the electrochemical inactivation of microorganisms. *Environmental science & technology*, *40*(19), 6117-6122.

JEPPESEN, B. (1994). Grey water Reuse. *Recycled Water Seminar.* AWWA NSW Branch: Newcastle: Newcastle City Hall Proceedings.

JIA, H. P., DREYER, D. R., & BIELAWSKI, C. W. (2011). C–H oxidation using graphite oxide. *Tetrahedron*, *67*(24), 4431-4434.

JIMENEZ, B., AND ASANO, T. (2008). Water reclamation and reuse around the world. *Water reuse: an international survey of current practice, issues and needs*, (20), 3.

JÜTTNER, K., GALLA, U., & SCHMIEDER, H. (2000). Electrochemical approaches to environmental problems in the process industry. *Electrochimica Acta*, *45*(15), 2575-2594.

KADIRVELU, K., THAMARAISELVI, K., & NAMASIVAYAM, C. (2001). Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresource Technology*, *76*(1), 63-65.

KARIMI-JASHNI, A., & NARBAITZ, R. M. (2005). Electrochemical reactivation of granular activated carbon: Effect of electrolyte mixing. *Journal of environmental engineering*, *131*(3), 443-449.

KAUR, T. (2010). *Charecterization and Treatability Studies on Grey Water of Domestic Activites* (Doctoral dissertation, THAPAR UNIVERSITY).

KELSALL, G. H. (1984). Hypochlorite electro-generation. I. A parametric study of a parallel plate electrode cell. *Journal of applied electrochemistry*, *14*(2), 177-186.

KERWICK, M. I., REDDY, S. M., CHAMBERLAIN, A. H. L., & HOLT, D. M. (2005). Electrochemical disinfection, an environmentally acceptable method of drinking water disinfection?. *Electrochimica Acta*, *50*(25), 5270-5277.

KHELIFA, A., MOULAY, S., & NACEUR, A. W. (2005). Treatment of metal finishing effluents by the electroflotation technique. *Desalination*, *181*(1), 27-33.

KIM, J., SONG, I., OH, H., JONG, J., PARK, J. & CHOUNG, Y. (2009). A laboratory-scale graywater treatment system based on a membrane filtration and oxidation process—characteristics of graywater from a residential complex. *Desalination,* 238**,** 347-357.

KIM, S., KIM, T. H., PARK, C., & SHIN, E. B. (2003). Electrochemical oxidation of polyvinyl alcohol using a RuO 2Ti anode. *Desalination*, *155*(1), 49-57.

KOLACZKOWSKI, S. T., PLUCINSKI, P., BELTRAN, F. J., RIVAS, F. J., & MCLURGH, D. B. (1999). Wet air oxidation: a review of process technologies and aspects in reactor design. *Chemical Engineering Journal*, *73*(2), 143-160.

KRAFT, A., STADELMANN, M., BLASCHKE, M., KREYSIG, D., SANDT, B., SCHRÖDER, F., & RENNAU, J. (1999). Electrochemical water disinfection Part I: Hypochlorite production from very dilute chloride solutions. *Journal of Applied Electrochemistry*, *29*(7), 859-866.

KRSTAJIĆ, N., NAKIĆ, V., & SPASOJEVIĆ, M. (1987). Hypochlorite production. I. A model of the cathodic reactions. *Journal of applied electrochemistry*, *17*(1), 77-81.

KUHN, A. T. (1971). Electrolytic decomposition of cyanides, phenols and thiocyanates in effluent streams—a literature review. *Journal of Applied Chemistry and Biotechnology*, *21*(2), 29-34.

KULKARNI, S., AND KAWARE, J. (2014). Regeneration and Recovery in Adsorption- A Review. International Journal of Innovative Science, Engineering & Technology, 8(1), 61-64.

KUOKKANEN, V., KUOKKANEN, T., RÄMÖ, J., & LASSI, U. (2013). Recent Applications of Electrocoagulation in Treatment of Water and Wastewater—A Review. *Green and Sustainable Chemistry*, *3*, 89.

KUSMARTSEV, F. V., WU, W. M., PIERPOINT, M. P., & YUNG, K. C. (2014). Application of Graphene within Optoelectronic Devices and Transistors. *arXiv preprint arXiv:1406.0809*.

LAAK, R. (1974). Relative pollution strengths of undiluted waste materials discharged in households and the dilution waters used for each. In: J. H. T. Winneberger, Manual of grey water treatment practice. Michigan, USA: Ann Arbor Science, 68-78.

LAAK, R. (1980). Wastewater engineering design for unsewered areas. Ann Arbor Science.

LAGERGREN, S. (1898). About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar,* 24**,** 1-39.

LAINE, A. T. 2001. Technologies for grey water recycling in buildings. PhD thesis, *Cranfield University*.

LAMINE, M., BOUSSELMI, L. & GHRABI, A. (2007). Biological treatment of grey water using sequencing batch reactor. *Desalination,* 215**,** 127-132.

LAZAROVA, V., HILLS, S., & BIRKS, R. (2003). Using recycled water for non-potable, urban uses: a review with particular reference to toilet flushing. *Water Supply*, *3*(4), 69-77.

LE LEUCH, L. M., & BANDOSZ, T. J. (2007). The role of water and surface acidity on the reactive adsorption of ammonia on modified activated carbons. *Carbon*, *45*(3), 568-578.

LEE, H. J., SARFERT, F., STRATHMANN, H., & MOON, S. H. (2002). Designing of an electrodialysis desalination plant. *Desalination*, *142*(3), 267-286.

LEE, H. J., OH, S. J., & MOON, S. H. (2003). Recovery of ammonium sulfate from fermentation waste by electrodialysis. *Water Research*, *37*(5), 1091-1099.

LEIDL, C. M., & LUBITZ, W. D. (2009). Comparing domestic water heating technologies. *Technology in Society*, *31*(3), 244-256.

LEHR, J. H. (2005). *Water encyclopedia*. John Wiley & Sons.

LENG, C. C., & PINTO, N. G. (1996). An investigation of the mechanisms of chemical regeneration of activated carbon. *Industrial & engineering chemistry research*, *35*(6), 2024-2031.

LESJEAN, B. & GNIRSS, R. (2006). Grey water treatment with a membrane bioreactor operated at low SRT and low HRT. *Desalination,* 199**,** 432-434.

LI, F., WICHMANN, K., GULYAS, H. & OTTERPOHL, R. (2007). TREATMENT OF HOUSEHOLD GREY WATER WITH A SUBMERGED UF MEMBRANE FILTRATION SYSTEM. *International Conference on Sustainable Sanitisation: Food and Water Security for Latin America*.

LI, F., WICHMANN, K., & OTTERPOHL, R. (2009). Review of the technological approaches for grey water treatment and reuses. *Science of the Total Environment*, *407*(11), 3439-3449.

LI, L., QUINLIVAN, P. A., & KNAPPE, D. R. (2002). Effects of activated carbon surface chemistry and pore structure on the adsorption of organic contaminants from aqueous solution. *Carbon*, *40*(12), 2085-2100.

LI, X., ZHANG, C., & LIU, J. (2010). Adsorption of oil from waste water by coal: characteristics and mechanism. *Mining Science and Technology (China)*, *20*(5), 778-781.

LIGMAN, K., HUTZLER, N., & BOYLE, W. C. (1974). Household wastewater characterisation. Journal of the Environmental Engineering Division, American Society of Civil Engineers, 100 (EE1), 201-213.

LIN, S. H., SHYU, C. T., & SUN, M. C. (1998). Saline wastewater treatment by electrochemical method. *Water Research*, *32*(4), 1059-1066.

LIN, C. J., LO, S. L., KUO, C. Y., & WU, C. H. (2005). Pilot-scale electrocoagulation with bipolar aluminum electrodes for on-site domestic greywater reuse. *Journal of environmental engineering*, *131*(3), 491-495.

LIU, R., HUANG, X., CHEN, L., WEN, X. & QIAN, Y. (2005). Operational performance of a submerged membrane bioreactor for reclamation of bath wastewater. *Process Biochemistry,* 40**,** 125-130.

LIU, B., ZENG, L., MAO, J., & REN, Q. (2010). Simulation of levulinic acid adsorption in packed beds using parallel pore/surface diffusion model. *Chemical Engineering & Technology*, *33*(7), 1146-1152.

LIU, L., FU, L., & ZHANG, S. (2014). The design and analysis of two exhaust heat recovery systems for public shower facilities. *Applied Energy*, *132*, 267-275

LOFRANO, G. & BROWN, J. (2010). Wastewater management through the ages: A history of mankind. *Science of the Total Environment,* 408**,** 5254-5264.

MAEDA, Y., OKEMOTO, Y., & INAGAKI, M. (1985). Electrochemical Formation of Graphite-Sulfuric Acid Intercalation Compounds on Carbon Fibers. *Journal of The Electrochemical Society*, *132*(10), 2369-2372.

MAEDA, Y., TOUZAIN, P., & BONNETAIN, L. (1988). Electrochemical formation of graphite intercalation compound in magnesium chloride-dimethylsulphoxide solution. *Synthetic metals*, *24*(3), 267-270.

MALIK, P. K. (2004). Dye removal from wastewater using activated carbon developed from sawdust: adsorption equilibrium and kinetics. *Journal of Hazardous Materials*, *113*(1), 81-88.

MANDAL, D., LABHASETWAR, P., DHONE, S., DUBEY, A. S., SHINDE, G., & WATE, S. (2011). Water conservation due to greywater treatment and reuse in urban setting with specific context to developing countries. *Resources, Conservation and Recycling*, *55*(3), 356-361.

MANISANKAR, P., VISWANATHAN, S., & RANI, C. (2003). Electrochemical treatment of distillery effluent using catalytic anodes. *Green chemistry*, *5*(2), 270-274.

MARCH, J. G., GUAL, M., & OROZCO, F. (2004). Experiences on greywater re-use for toilet flushing in a hotel (Mallorca Island, Spain). *Desalination*, *164*(3), 241-247.

MARCH, J. G., & GUAL, M. (2009). Studies on chlorination of greywater. *Desalination*, *249*(1), 317-322.

MARSELLI, B., GARCIA-GOMEZ, J., MICHAUD, P. A., RODRIGO, M. A., & COMNINELLIS, C. (2003). Electrogeneration of hydroxyl radicals on boron-doped diamond electrodes. *Journal of The Electrochemical Society*, *150*(3), D79-D83.

MARTÍNEZ-HUITLE, C. A. (2004). Direct and indirect electrochemical oxidation of organic pollutants. Unpublished PhD thesis. University of Ferrara (Italy).

MARTINEZ-HUITLE, C. A., & FERRO, S. (2006). Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chemical Society Reviews*, *35*(12), 1324-1340.

MARTINEZ-HUITLE, C. A., & BRILLAS, E. (2008). Electrochemical alternatives for drinking water disinfection. *Angewandte Chemie International Edition*, *47*(11), 1998-2005.

MASSCHELEIN, W. (1992). *Unit processes in drinking water treatment,* New York, Marcel Dekker Inc.

MATSUO, Y., WATANABE, K., FUKUTSUKA, T., & SUGIE, Y. (2003). Characterization of n-hexadecylalkylamine-intercalated graphite oxides as sorbents. *Carbon*, *41*(8), 1545-1550.

MCCABE, W. L., SMITH, J. C., & HARRIOTT, P. (1993). *Unit operations of chemical engineering*. New York: McGraw-Hill.

MCKAY, G. (1996). *Use of Adsorbents for the Removal of Pollutants from Wastewater*. CRC press.

MEHTA, M. P. & FLORA, J. R. V. (1997). Effects of electrochemical treatment of granular activated carbon on surface acid groups and the adsorptive capacity for phenol. *Water research,* 31**,** 2171-2176.

MENG, H., PENG, C., SONG, S., & DENG, D. (2004). Electro-regeneration mechanism of ion-exchange resins in electrodeionization. *Surface Review and Letters*, *11*(06), 599-605.

MERZOUK, B., GOURICH, B., SEKKI, A., MADANI, K., & CHIBANE, M. (2009). Removal turbidity and separation of heavy metals using electrocoagulation–electroflotation technique: A case study. *Journal of hazardous materials*, *164*(1), 215-222.

METCALF, E. (2003). Inc., Wastewater Engineering, Treatment and Reuse. *New York: McGraw-Hill*.

MOHAMMED, F. M. (2011). *Modelling and design of water treatment processes using adsorption and electrochemical regeneration* (Doctoral dissertation, University of Manchester).

MOHAN, D., GUPTA, V. K., SRIVASTAVA, S. K., & CHANDER, S. (2000). Kinetics of mercury adsorption from wastewater using activated carbon derived from fertilizer waste. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *177*(2), 169-181.

MOLDEN, D. (2007). Water for food, water for life: A comprehensive assessment of water management in agriculture. London: *Earthscan, and Colombo: International Water Management Institute*, 62-63.

MOLLAH, M. Y., MORKOVSKY, P., GOMES, J. A., KESMEZ, M., PARGA, J., & COCKE, D. L. (2004). Fundamentals, present and future perspectives of electrocoagulation. *Journal of Hazardous Materials*, *114*(1), 199-210.

MONTELEONE, M., YEUNG, H. & SMITH, R. 2007. A review of Ancient Roman water supply exploring techniques of pressure reduction. p.2.

MOREL, A., & DIENER, S. (2006). Greywater management in low and middle income countries. Review of Different Treatment Systems for Households or Neighbourhoo*ds*. Dubendorf, Switzerland. *Swiss Federal Institution of Aquatic Science and Technology (Eawag)*.

MORAES DE JÚNIOR, D., LIA, L. R. B., PEREIRA, F., BONFANTI, O., & SILVA, E. L. (2000). Small Low-Cost Equipment and Fast Experiments at a unit Operations Laboratory: Adsorption/Breakthrough Curves.

MOURAD, K. A., BERNDTSSON, J. C., & BERNDTSSON, R. (2011). Potential fresh water saving using greywater in toilet flushing in Syria. *Journal of environmental management*, *92*(10), 2447-2453.

MRAZ, R., & KRÝSA, J. (1994). Long service life IrO2/Ta2O5 electrodes for electrofloatation. *Journal of applied electrochemistry*, *24*(12), 1262-1266.

MUELLER, S. A., KIM, B. R., ANDERSON, J. E., GASLIGHTWALA, A., SZAFRANSKI, M. J., & GAINES, W. A. (2003). Removal of oil and grease and chemical oxygen demand from oily automotive wastewater by adsorption after chemical de-emulsification. *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management*, *7*(3), 156-162.

MUNDALE, V. D., JOGLEKAR, H. S., KALAM, A., & JOSHI, J. B. (1991). Regeneration of spent activated carbon by wet air oxidation. *The Canadian Journal of Chemical Engineering*, *69*(5), 1149-1159.

MURPHY, O. J., DUNCAN HITCHENS, G., KABA, L., & VEROSTKO, C. E. (1992). Direct electrochemical oxidation of organics for wastewater treatment. *Water Research*, *26*(4), 443-451.

NAKAJIMA, N., NAKANO, T., HARADA, F., TANIGUCHI, H., YOKOYAMA, I., HIROSE, J., & SANO, K. (2004). Evaluation of disinfective potential of reactivated free chlorine in pooled tap water by electrolysis. *Journal of microbiological methods*, *57*(2), 163-173.

NAMASIVAYAM, C., & KAVITHA, D. (2002). Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. *Dyes and pigments*, *54*(1), 47-58.

NARBAITZ, R. M., AND CEN, J. (1994). Electrochemical regeneration of granular activated carbon. *Water Research*, *28*(8), 1771-1778.

NARBAITZ, R. M., AND KARIMI-JASHNI, A. (2009). Electrochemical regeneration of granular activated carbons loaded with phenol and natural organic matter. *Environmental technology*, *30*(1), 27-36.

NAUMCZYK, J., SZPYRKOWICZ, L., & ZILIO-GRANDI, F. (1996). Electrochemical treatment of textile wastewater. *Water Science and Technology*, *34*(11), 17-24.

NELSON, N. (2002). Electrochemical destruction of organic hazardous wastes. *Platinum Metals Review*, *46*(1), 18-23.

NEMR, A. E., ABDELWAHAB, O., EL-SIKAILY, A., & KHALED, A. (2009). Removal of direct blue-86 from aqueous solution by new activated carbon developed from orange peel. *Journal of hazardous materials*, *161*(1), 102-110.

NI, L., LAU, S. K., LI, H., ZHANG, T., STANSBURY, J. S., SHI, J., & NEAL, J. (2012). Feasibility study of a localized residential grey water energy-recovery system. *Applied Thermal Engineering*, *39*, 53-62.

NKRUMAH-AMOAKO, K., ROBERTS, E. P., BROWN, N. W., & HOLMES, S. M. (2014). The effects of anodic treatment on the surface chemistry of a Graphite Intercalation Compound. *Electrochimica Acta*, *135*, 568-577.

NOEL, M., & SANTHANAM, R. (1998). Electrochemistry of graphite intercalation compounds. *Journal of power sources*, *72*(1), 53-65.

NOLDE, E. (2000). Greywater reuse systems for toilet flushing in multi-storey buildings–over ten years experience in Berlin. *Urban water*, *1*(4), 275-284.

NOLDE, E. (2005). Greywater recycling systems in Germany results, experiences and guidelines. *Water Science & Technology*, *51*(10), 203-210.

NOYES, R. (1994). *Unit operations in environmental engineering*. William Andrew.

OASIS DESIGN. (2009). *History of Graywater Regulation: Timeline of Evolving Gray Water Standards in California and US* [Online]. USA: Oasis design. Available: http://oasisdesign.net/grey water/law/history/index.htm [Accessed September 2012].

OFFICE OF THE QUEENSLAND PARLIAMENTARY COUNSEL. (2011). Queensland Plumbing and Wastewater Code. *Grey water use facilities.* Australia: Office of the Queensland Parliamentary Counsel.

OK, Y. S., YANG, J. E., ZHANG, Y. S., KIM, S. J., & CHUNG, D. Y. (2007). Heavy metal adsorption by a formulated zeolite-Portland cement mixture. *Journal of Hazardous Materials*, *147*(1), 91-96.

OLANIPEKUN, O., OYEFUSI, A., NEELGUND, G. M., & OKI, A. (2014). Adsorption of lead over graphite oxide. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, *118*, 857-860.

OLDHAM, K. B., & MYLAND, J. C. (1994). Fundamentals of Electrochemical Science. *Publisher: Academic Press, Inc., Published in: San Diego*, 328-332.

OTTOSON, J., & STENSTRÖM, T. A. (2003). Faecal contamination of greywater and associated microbial risks. *Water research*, *37*(3), 645-655.

OWEN, G., BANDI, M., HOWELL, J. A., & CHURCHOUSE, S. J. (1995). Economic assessment of membrane processes for water and waste water treatment. *Journal of membrane science*, *102*, 77-91.

OYA, A., MARSH, H., HEINTZ, E. A., & RODRIGUEZ-REINOSO, F. (1997). Introduction to carbon technologies. *Alicante: Universidad de Alicante, Secretariado de Publicaciones*, *561*.

ONYANGO, M. S., KOJIMA, Y., AOYI, O., BERNARDO, E. C. & MATSUDA, H. 2004. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *Journal of Colloid and Interface Science,* 279**,** 341–350.

ÖZMEN-MONKUL, B., & LERNER, M. M. (2010). The first graphite intercalation compounds containing tris (pentafluoroethyl) trifluorophosphate. *Carbon*, *48*(11), 3205-3210.

PALIN, A. T. (1957). The determination of free and combined chlorine in water by the use of diethyl-p-phenylene diamine. *Journal (American Water Works Association)*, 873-880.

PALMER, J., COOPER, I., CHENG, V., CAR, A. T., SUMMERTON, P., CE, R. M., & ECONOMETRICS, C. (2011). Great Britain's housing energy fact file 2011. *Department of Energy and Climate Change, London*.

PANIZZA, M., BOCCA, C., & CERISOLA, G. (2000). Electrochemical treatment of wastewater containing polyaromatic organic pollutants. *Water Research*, *34*(9), 2601-2605.

PANIZZA, M., ZOLEZZI, M., & NICOLELLA, C. (2006). Biological and electrochemical oxidation of naphthalenesulfonates. *Journal of Chemical Technology and Biotechnology*, *81*(2), 225-232.

PARSONS, S. A., BEDEL, C., & JEFFERSON, B. (2000). Chemical vs. Biological Treatment of Grey Water. In *Chemical Water and Wastewater Treatment VI* (pp. 383-392). Springer Berlin Heidelberg.

PATIL, R. K., SHENDE, B. W., & GHOSH, P. K. (1982). Designing a helical-coil heat exchanger. *Chemical Engineering*, *92*(24), 85-88.

PATTON, A., CRITTENDEN, B. D., & PERERA, S. P. (2004). Use of the linear driving force approximation to guide the design of monolithic adsorbents. *Chemical Engineering Research and Design*, *82*(8), 999-1009.

PENN, R., HADARI, M., & FRIEDLER, E. (2012). Evaluation of the effects of greywater reuse on domestic wastewater quality and quantity. *Urban Water Journal*, *9*(3), 137-148.

PEREZ, N. (2004). Electrochemistry and Corrosion Science (Information Technology: Transmission, Processing & Storage). 2004 Edition. Springer.

PERIĆ, J., TRGO, M., & VUKOJEVIĆ MEDVIDOVIĆ, N. (2004). Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. *Water Research*, *38*(7), 1893-1899.

PIDOU, M., MEMON, F. A., STEPHENSON, T., JEFFERSON, B., & JEFFREY, P. (2007). Greywater recycling: A review of treatment options and applications. *Proceedings of the ICE-Engineering Sustainability*, *160*(3), 119-131.

PIDOU, M., AVERY, L., STEPHENSON, T., JEFFREY, P., PARSONS, S. A., LIU, S., & JEFFERSON, B. (2008). Chemical solutions for greywater recycling. *Chemosphere*, *71*(1), 147-155.
PIERSON, H. O. (1994). *Handbook of carbon, graphite, diamonds and fullerenes: processing, properties and applications*. William Andrew.

POLCARO, A. M., VACCA, A., MASCIA, M., PALMAS, S., POMPEI, R., & LACONI, S. (2007). Characterization of a stirred tank electrochemical cell for water disinfection processes. *Electrochimica Acta*, *52*(7), 2595-2602.

POTTER, N. N., & HOTCHKISS, J. H. (1995). Unit operations in food processing. In *Food Science* (pp. 69-89). Springer US.

PRATHAPAR, S. A., JAMRAH, A., AHMED, M., AL ADAWI, S., AL SIDAIRI, S., & AL HARASSI, A. (2005). Overcoming constraints in treated greywater reuse in Oman. *Desalination*, *186*(1), 177-186.

PRIME, J., KHAN, S., & WILKES, E. (2014). Energy Consumption in the UK: Domestic Energy Consumption in the UK between 1970 and 2013. Department of Energy and Climate Change, UK.

PURAKAYASTHA, D., PAL, A., & BANDYOPADHYAY, M. (2005). Adsorbent selection for anionic surfactant removal from water. *Indian journal of chemical technology*, *12*(3), 281-284.

PYO, M., & MOON, I. S. (2005). Indirect electrochemical oxidation of phenol by Ce4+, controlling surface insulation of Au electrode. *Bull. Korean Chem. Soc*, *26*(6), 899.

QADIR, M., BAHRI, A., SATO, T., & AL-KARADSHEH, E. (2010). Wastewater production, treatment, and irrigation in Middle East and North Africa. *Irrigation and Drainage Systems*, *24*(1-2), 37-51.

QIU, H., LV, L., PAN, B.-C., ZHANG, Q.-J., ZHANG, W.-M. & ZHANG, Q.-X. (2009). Critical review in adsorption kinetic models. *Journal of Zhejiang University SCIENCE A,* 10**,** 716-724.

QUEENSLAND GOVERNMENT. (2007). Home Waterwise reaches $100 million Mark. Press release by Premier Beattie, 7 August 2007. Accessed from http://www.cabinet.qld.gov.au/MMS/StatementDisplaySingle.aspx?id=53332

RAJESHWAR, K. I. J. G., IBANEZ, J. G., & SWAIN, G. M. (1994). Electrochemistry and the environment. *Journal of Applied Electrochemistry*, *24*(11), 1077-1091.

RAMONA, G., GREEN, M., SEMIAT, R. & DOSORETZ, C. (2004). Low strength graywater characterization and treatment by direct membrane filtration. *Desalination,* 170**,** 241-250.

REDWOOD CITY. (2012). Redwood City Recycled Water Project. [online] Available at: http://www.redwoodcity.org/publicworks/water/recycling/index.html [Accessed 24 Nov. 2013].

ROCKSTRÖM, J., FALKENMARK, M., KARLBERG, L., HOFF, H., ROST, S., & GERTEN, D. (2009). Future water availability for global food production: the potential of green water for increasing resilience to global change. *Water Resources Research*, *45*(7).
ROSE, J. B., SUN, G. S., GERBA, C. P., & SINCLAIR, N. A. (1991). Microbial quality and persistence of enteric pathogens in graywater from various household sources. *Water Research*, *25*(1), 37-42.

RONEN, Z., GUERRERO, A., & GROSS, A. (2010). Greywater disinfection with the environmentally friendly Hydrogen Peroxide Plus (HPP). *Chemosphere*, *78*(1), 61-65.

RÜDORFF, W., STUMPP, E., SPRIESSLER, W., & SIECKE, F. W. (1963). Reactions of Graphite with Metal Chlorides. *Angewandte Chemie International Edition in English*, *2*(2), 67-73.

RUTHVEN, D. M. (1984). *Principles of adsorption and adsorption processes*. John Wiley & Sons.

SAN MIGUEL, G., LAMBERT, S. D., & GRAHAM, N. J. D. (2001). The regeneration of field-spent granular-activated carbons. *Water research*, *35*(11), 2740-2748.

SANCHEZ, M., RIVERO, M. & ORTIZ, I. (2010). Photocatalytic oxidation of grey water over titanium dioxide suspensions. *Desalination,* 262**,** 141-146.

SANTALA, E., UOTILA, J., ZAITSEV, G., ALASIURUA, R., TIKKA, R. & TENGVALL, J. (1998). Microbiological grey water treatment and recycling in an apartment building. *AWT98-Advanced Wastewater Treatment, Recycling and Reuse: Milan***,** 14-16.

SANTANA, M. H., DE FARIA, L. A., & BOODTS, J. F. (2005). Electrochemical characterisation and oxygen evolution at a heavily boron doped diamond electrode. *Electrochimica acta*, *50*(10), 2017-2027.

SARIOGLU, M. (2005). Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. *Separation and purification technology*, *41*(1), 1-11.

SAVALL, A. (1995). Electrochemical treatment of industrial organic effluents. *Chimia International Journal for Chemistry*, *49*(1-2), 23-27.

SCHULTE, P. (2014). Defining Water Scarcity, Water Stress, and Water Risk: It's Not Just Semantics - Pacific Institute. [ONLINE] Available at: http://pacinst.org/water-definitions/. [Accessed 28 October 2014].

SCIALDONE, O., RANDAZZO, S., GALIA, A., & SILVESTRI, G. (2009). Electrochemical oxidation of organics in water: role of operative parameters in the absence and in the presence of NaCl. *Water research*, *43*(8), 2260-2272.

SEMERJIAN, L., & AYOUB, G. M. (2003). High-pH–magnesium coagulation–flocculation in wastewater treatment. *Advances in Environmental Research*, *7*(2), 389-403.

SERIKAWA, R. M., ISAKA, M., SU, Q., USUI, T., NISHIMURA, T., SATO, H., & HAMADA, S. (2000). Wet electrolytic oxidation of organic pollutants in wastewater treatment. *Journal of applied electrochemistry*, *30*(7), 875-883.

SHIN, E. W., HAN, J. S., JANG, M., MIN, S. H., PARK, J. K. & ROWELL, R. M. (2004). Phosphate Adsorption on Aluminum-Impregnated Mesoporous Silicates: Surface Structure and Behavior of Adsorbents. *Environmental Science and Technology,* 38**,** 912–917.

SIEGRIST, R. L., WITT, M. D., & BOYLE, W. C. (1976). *The characteristics of rural household wastewater*. Small Scale Waste Management Project, University of Wisconsin--Madison and University of Wisconsin—Extension, 533-548.

SIROKMAN, G., MASTALIR, A., BARTÓK, M., SCHAY, Z., & GUCZI, L. (1990). Structure and catalytic activity of copper, nickel, and platinum graphimets prepared from graphite intercalation compounds. *Carbon*, *28*(1), 35-42.

SISTAT, P., KOZMAI, A., PISMENSKAYA, N., LARCHET, C., POURCELLY, G., & NIKONENKO, V. (2008). Low-frequency impedance of an ion-exchange membrane system. *Electrochimica Acta*, *53*(22), 6380-6390.

SKOWROŃSKI, J. M., & KRAWCZYK, P. (2004). Electrooxidation of phenol at exfoliated graphite electrode in alkaline solution. *Journal of Solid State Electrochemistry*, *8*(6), 442-447.

ŚLIWIŃSKA-BARTKOWIAK, M., DROZDOWSKI, H., KEMPIŃSKI, M., JAŻDŻEWSKA, M., LONG, Y., PALMER, J. C., & GUBBINS, K. E. (2012). Structural analysis of water and carbon tetrachloride adsorbed in activated carbon fibres. *Physical Chemistry Chemical Physics*, *14*(19), 7145-7153.

ŠOSTAR-TURK, S., PETRINIĆ, I., & SIMONIČ, M. (2005). Laundry wastewater treatment using coagulation and membrane filtration. *Resources, Conservation and Recycling*, *44*(2), 185-196.

SOUTHERN ELECTRIC (2015). Prices & Tariff Information. [Online] Available at: https://www.southern-electric.co.uk/ourprices/current/?ekfxmensel=663_665_665&postcode=se12 8ug [Accessed: 22nd March 2015].

SOUTHEAST WATER. (2007).http://apps.southeastwater.com.au/waterlevels/reservoirs.asp Standards Australia / Standards New Zealand. 2000. AS/NZS 1547:2000 *On-site Domestic wastewater Management*.

SOUTHERN WATER (2015) Our charges. [Online] Available at: https://www.southernwater.co.uk/our-charges [Accessed: 22nd March 2015].

STEELE, D. F., CRAIG, D. R., CAMPBELL, J. D., RICHARDSON, D., & QUINN, J. D. (1990). Low-temperature destruction of organic waste by electrochemical oxidation. *Process Safety and Environmental Protection*, *68*, 115-21.

STRATHMANN, H., KROL, J. J., RAPP, H. J., & EIGENBERGER, G. (1997). Limiting current density and water dissociation in bipolar membranes. *Journal of Membrane Science*, *125*(1), 123-142.

SUENDO, V., ETO, R., OSAKI, T., HIGA, M., & TANIOKA, A. (2001). Ionic environmental effect on the time-dependent characteristics of membrane potential in a bipolar membrane. *Journal of colloid and interface science*, *240*(1), 162-171.

SURENDRAN, S., & WHEATLEY, A. D. (1998). Grey-water reclamation for non-potable re-use. *Water and Environment Journal*, *12*(6), 406-413.

TAIWO, E. A., & ADESINA, A. (2005). Electrochemical regeneration of a native activated carbon. *Chemical and biochemical engineering quarterly*, *19*(3), 269-273.
TAKY, M., POURCELLY, G., & GAVACH, C. (1992). Polarization phenomena at the interfaces between an electrolyte solution and an ion exchange membrane: Part II. Ion transfer with an anion exchange membrane. *Journal of Electroanalytical Chemistry*, *336*(1), 195-212.

TANAKA, Y. (2004). Concentration polarization in ion-exchange membrane electrodialysis: The events arising in an unforced flowing solution in a desalting cell. *Journal of membrane science*, *244*(1), 1-16.

TAYLOR, R. M., AND PHELAN, D. M. (2003). *U.S. Patent No. 6,627,450*. Washington, DC: U.S. Patent and Trademark Office.

TCHOBANOGLOUS, G., BURTON, F. L., STENSEL, D. H. (2003). Wastewater Engineering: Treatment and Reuse. 4th ed. New York: McGraw-Hill. 1138-1162.

TEKKEN, V., & KROPP, J. P. (2012). Climate-driven or human-induced: Indicating severe water scarcity in the Moulouya River Basin (Morocco). *Water*, *4*(4), 959-982.

THE WORLD BANK. (2011). Water Reuse in the Arab World: From Principle to Practice. A Summary of Proceedings; Wastewater Management in the Arab World. [Online] Available at: http://water.worldbank.org/sites/water.worldbank.org/files/publication/Water-Reuse-Arab-World-From-Principle%20-Practice.pdf. [Accessed 13 June 2013].

THOMAS, H. C. (1944). Heterogeneous ion exchange in a flowing system. *Journal of the American Chemical Society*, *66*(10), 1664-1666.

THOMAS, W. J., & CRITTENDEN, B. D. (1998). *Adsorption technology and design*. Butterworth-Heinemann.

TIEN, C. (1994). *Adsorption calculations and modeling* (Vol. 244). Boston: Butterworth-Heinemann.

TOYODA, M., & INAGAKI, M. (2000). Heavy oil sorption using exfoliated graphite: New application of exfoliated graphite to protect heavy oil pollution. *Carbon*, *38*(2), 199-210.

TRIPATHI, N. (2013). Water Scarcity: An Alarming Global Concern, Green Earth Citizen. [ONLINE] Available at: http://greenearthcitizen.org/water-scarcity-an-alarming-global-concern/. [Accessed 28 October 2014].

TUFVESSON, A. (2009). *Graywater treatment and technology* [Online]. Austrialia: World Publishing Info. Available: http://www.worldplumbinginfo.com/grey water-treatment-and-technology [Accessed September 2012].

TWUMASI, S. K. (2002) Catalytic Investigations of CO and NO Reactions Applying Exfoliated Graphite Intercalation Compounds of AlCl3, CuCl2, MoOCl3, FeCl3, and Ce (IV) nitrate.

UBBELOHDE, A. R., & LEWIS, F. A. (1960). *Graphite and its crystal compounds* (p. 114). Oxford: Clarendon Press.

UNIVERSITY OF WISCONSIN-MADISON. (1978). Management of Small Wastewater Flows. EPA-600/7-78-173. U.S. Environmental Protection Agency, Office of Research and Development, Municipal Environmental Research Laboratory (MERL) Cincinnati, OH.

USHIJIMA, K., ITO, K., ITO, R. & FUNAMIZU, N. (2012). Grey water treatment by slanted soil system. *Ecological Engineering*.

VELEGRAKI, T., BALAYIANNIS, G., DIAMADOPOULOS, E., KATSAOUNIS, A., & MANTZAVINOS, D. (2010). Electrochemical oxidation of benzoic acid in water over boron-

doped diamond electrodes: Statistical analysis of key operating parameters, kinetic modeling, reaction by-products and ecotoxicity. *Chemical Engineering Journal*, *160*(2), 538-548.

VICKERS, A. (2001). Handbook of water use and conservation: homes, landscapes, businesses, industries, farms. *Water-Plow Press, Amherst, Massachusetts*.

VIDIC, R. D., SUIDAN, M. T., SORIAL, G. A., & BRENNER, R. C. (1993). Molecular oxygen and the adsorption of phenols—effect of functional groups. *Water environment research*, *65*(2), 156-161.

VIEIRA, F., CISNEROS, I., ROSA, N. G., TRINDADE, G. M., & MOHALLEM, N. D. S. (2006). Influence of the natural flake graphite particle size on the textural characteristic of exfoliated graphite used for heavy oil sorption. *Carbon*, *44*(12), 2590-2592.

VIZHEMEHR, A. K., AND HAGHIGHAT, F. (2014). Modeling of gas-phase filter model for high-and low-challenge gas concentrations. *Building and Environment*, *80*, 192-203.

VON OEPEN, B., KÖRDEL, W., & KLEIN, W. (1991). Sorption of nonpolar and polar compounds to soils: processes, measurements and experience with the applicability of the modified OECD-Guideline 106. *Chemosphere*, *22*(3), 285-304.

VUORINEN, H., JUUTI, P. & KATKO, T. (2007). History of water and health from ancient civilizations to modern times. *Water Science & Technology: Water Supply,* 7**,** 49-57.

WANG, C. T. (2003). Decolorization of congo red with three-dimensional flow-by packed-bed electrodes. *Journal of Environmental Science and Health, Part A*, *38*(2), 399-413.

WANG, C. T., CHOU, W. L., & KUO, Y. M. (2009). Removal of COD from laundry wastewater by electrocoagulation/electroflotation. *Journal of hazardous materials*, *164*(1), 81-86.

WANG, J., WANG, S., & JIN, M. (2000). A study of the electrodeionization process—high-purity water production with a RO/EDI system. *Desalination*, *132*(1), 349-352.

WANG, S., ZHU, Z. H., COOMES, A., HAGHSERESHT, F., & LU, G. Q. (2005). The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater. *Journal of Colloid and Interface Science*, *284*(2), 440-446.

WANG, S., LI, H., & XU, L. (2006). Application of zeolite MCM-22 for basic dye removal from wastewater. *Journal of colloid and interface science*, *295*(1), 71-78.

WANG, F., YI, J., WANG, Y., WANG, C., WANG, J., & XIA, Y. (2014). Graphite Intercalation Compounds (GICs): A New Type of Promising Anode Material for Lithium-Ion Batteries. *Advanced Energy Materials*, *4*(2).

WARD, M. (2000). *Treatment of Domestic Grey water Using Biological and Membrane Separation Techniques.* MPhil thesis, Cranfield University.

WATER REUSE ASSOCIATION. (2008). What is Water Reuse? - Who Is Reusing? A Thirsty Planet. [online] Available at: http://www.athirstyplanet.com/be_informed/what_is_water_reuse/who-is-reusing [Accessed 20 Nov. 2013].

WEAVER, J. C., & CHIZMADZHEV, Y. A. (1996). Theory of electroporation: a review. *Bioelectrochemistry and bioenergetics*, *41*(2), 135-160.

WEBER JR, W. J., MCGINLEY, P. M., & KATZ, L. E. (1991). Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport. *Water Research*, *25*(5), 499-528.

WENG, C. H., & HSU, M. C. (2008). Regeneration of granular activated carbon by an electrochemical process. *Separation and Purification Technology*, *64*(2), 227-236.

WICKSTEAD, F. A. (2011). *Quantifying the benefits of grey water systems.* Masters of Science, Georgia Institute of Technology.

WIDIASTUTI, N., WU, H., ANG, H. M., & ZHANG, D. (2011). Removal of ammonium from greywater using natural zeolite. *Desalination*, *277*(1), 15-23.

WINNEBERGER, J. H. T. (1974). *Manual of grey water treatment practice*, Ann Arbor Science.

WINWARD, G. P., AVERY, L. M., STEPHENSON, T., & JEFFERSON, B. (2008a). Chlorine disinfection of grey water for reuse: Effect of organics and particles. *Water Research*, *42*(1), 483-491.

WINWARD, G. P., AVERY, L. M., STEPHENSON, T., & JEFFERSON, B. (2008b). Essential oils for the disinfection of grey water. *Water research*, *42*(8), 2260-2268.

WHITE, G. C. (2005). *Handbook of chlorination and alternative disinfectants*. Van Nostrand Reinhold, New York.

WHITEHEAD, J.H. AND PATTERSON, R.A. (2007). Assessing sustainable grey water reuse and application rates in Patterson, R.A. & Jones, M.J. (Eds) *Innovation and Technology for On-site Systems*. Proceedings of On-site '07 conference. 25-27 September 2007. Lanfax Laboratories. Armidale. pp 331-338.

WHITTINGHAM, M. S., ZAVALIJ, P., NGALA, K., & ZHANG, F. (2000). 25 Years of Intercalation Chemistry for Battery Materials. In *Intercalation Compounds for Battery Materials: Proceedings of the International Symposium* (p. 15). The Electrochemical Society.

WORCH, E. (2012). *Adsorption technology in water treatment: fundamentals, processes, and modeling*. Walter de Gruyter.

WORLD HEALTH ORGANISATION. (1973). Reuse of effluents: Methods of Wastewater Treatmend and Health Safeguards. *World Health Organisation Technical report.* Switzerland.

WORLD HEALTH ORGANISATION. (1989). Health guidelines for the use of wastewater in agriculture and aquaculture. *World Health Organisation Technical report.* Switzerland.

WORLD HEALTH ORGANISATION. (2006). WHO Guidelines for the Safe use of Wastewater, Excreta and Grey water. *Policy and regulatory aspects.* France.

WU, J., HE, F., XU, D., WANG, R., ZHANG, X., XIAO, E., & WU, Z. (2011). Phosphorus removal by laboratory-scale unvegetated vertical-flow constructed wetland systems using anthracite, steel slag and related blends as substrate.

WWF (WORLD WIDE FUND). (2014). Water Scarcity Threats. WWF. [ONLINE] Available at: https://www.worldwildlife.org/threats/water-scarcity. [Accessed 14 April 2014].

XU, Z., CAI, J. G., & PAN, B. C. (2013). Mathematically modeling fixed-bed adsorption in aqueous systems. *Journal of Zhejiang University SCIENCE A*, *14*(3), 155-176.

YOON, Y. H., & NELSON, J. H. (1984). Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life. *The American Industrial Hygiene Association Journal*, *45*(8), 509-516.

ZALOUM, C., LAFRANCE, M., & GUSDORF, J. (2007). Drain water heat recovery characterization and modeling. *Ottawa: Sustainable Buildings and Communities Natural Resources Canada*, 38-40.

ZALESKI, H. (1985). Energy Bands of Acceptor-Type Graphite Intercalation Compounds.

ZHANG, H. (2002). Regeneration of exhausted activated carbon by electrochemical method. *Chemical Engineering Journal*, *85*(1), 81-85.

ZOR, S. (2004). Investigation of the adsorption of anionic surfactants at different pH values by means of active carbon and the kinetics of adsorption. *Journal of the Serbian Chemical Society*, *69*(1), 25-32.

ZUO, Q., CHEN, X., LI, W., & CHEN, G. (2008). Combined electrocoagulation and electroflotation for removal of fluoride from drinking water. *Journal of hazardous materials*, *159*(2), 452-457.